



SPAWAR
Systems Center
San Diego

TECHNICAL REPORT 1918
August 2004

Use of Data on Contaminant/Sediment Interactions to Streamline Sediment Assessment and Management

S. E. Apitz
B. P. Ayers
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ADMINISTRATIVE INFORMATION

This report was prepared for the Naval Facilities Engineering Command, Y0187 Navy Pollution Abatement Ashore Technology Demonstration/Validation Program by the Applied Technology Test & Evaluation Branch (Code 2745) of the of the Ocean Systems Division (Code 274) of Space and Naval Warfare (SPAWAR) Systems Center, San Diego.

Released by
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EXECUTIVE SUMMARY

This report presents successful ways to use biogeochemical characterization data to optimize sediment site assessment and management. Appropriate data will help risk assessors and managers guide, define, negotiate, and comply with current regulatory and U.S. Navy guidance, as well as achieve cost reduction and more effective remedies. In most cases, this report is consistent with the recently published U.S. Environmental Protection Agency (EPA) “Principles for Managing Contaminated Sediment Risks at Hazardous Waste Sites” (U.S. EPA, 2002). Sections of this guidance should help manage sediments in line with these principles. As with every issue that is complex in regulatory and technical terms, all steps of the process should be designed and carried out in close collaboration and communication with all parties. This report highlights many successful aspects of contaminated sediment assessment and management. It provides site owners with examples of how to use site-specific data to compare site, background, and regional sediment signatures to address risk, determine responsibility for inputs, rank sites, and prioritize management; to help bridge the gap between remedial investigations and feasibility studies; and to provide site owners with the tools to rapidly determine what sediment management approaches are feasible for contaminated sediments at their sites—and to use site data to evaluate, communicate, and negotiate management choices. The approach of this report is to highlight some major uses for data on contaminant/sediment geochemical interactions in the assessment and management of contaminated sediments. It is not an exhaustive review of all potentialities, but it does provide many examples, case studies, and standard operating procedures (SOPs) that should aid Remedial Project Managers (RPMs), risk assessors, and managers in using site data to evaluate, negotiate, and select management strategies.

This report is organized into four sections, a reference list, and two appendices. The report also provides hyperlinks to relevant Web sites and documents.

Section 1, Introduction, presents general issues regarding contaminated marine sediments and a brief introduction to some critical factors in sediment assessment and management.

Section 2, Maximizing Data Use for Contaminated Sediment Assessment and Management, discusses many approaches to sediment data use that can help streamline the sediment assessment and management process.

Section 3, Biogeochemical Characterization within the U.S. Navy Ecological Risk Assessment Framework, highlights some major uses for data on contaminant/sediment geochemical interactions in the assessment and management of contaminated sediments within the U. S. Navy’s tiered approach. Case studies and examples illustrate various approaches and techniques.

Section 4, Use of Sediment Data in the Evaluation of Remedial Options, discusses how site-specific sediment/contaminant distribution data can help evaluate the potential risks and benefits of various remedial options, spanning the continuum from No Further Action (NFA) to In-Place Remedies to active removal and treatment. Several case studies, examples, and SOPs are presented.

The Reference section provides references and Web site addresses for information provided in the cited document.

Appendix A, Sediment Characterization Standard Operating Procedures, provides step-by-step procedures to address various issues such as Mass Allocation of Sediment and Contaminant, Potential Effects of Long-Term Mixing on COPC Concentrations, Size Fraction Contributions to Bulk Metal Concentration, and the Effect of Pre-Treatment on Overall Treatment Cost.

Appendix B, Sediment Characterization Flowcharts, provides a question and answer guide to using data to address various aspects of the ERA process.

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ABBREVIATIONS AND ACRONYMS

AET	Apparent Effects Level
Al	Aluminum
ARCS	Assessment and Remediation of Contaminated Sediment
AVS	Acid-Volatile Sulfides
BEDS	Biological Effects Database
BERA	Baseline Risk Assessment
BFSD	Benthic Flux Sampling Device
BRAC	Base Realignment and Closure
Cd	Cadmium
CDF	Confined Disposal Facility
CERLA	Comprehensive Environmental Response, Compensation, and Liability Act
CHC	Chlorinated Hydrocarbon Compound
CNO	Chief of Naval Operations
COC	Contaminant of Concern
COPC	Contaminant of Potential Concern
Cr	Chromium
Cs	Cesium
CSM	Conceptual Site Model
Cu	Copper
DoD	Department of Defense
DDT	Dichlorodiphenyltrichloroethane
DQO	Data Quality Objective
EPA	Environmental Protection Agency
ERA	Ecological Risk Assessment
ER-L	Effects Range Low
ER-M	Effects Range Medium
EVS	Environmental Consultants
Fe	Iron
FS	Feasibility Study
HCB	Hexachlorobenzene
HMWPAH	High Molecular Weight Polycyclic Aromatic Hydrocarbon
HQ	Hazard Quotient
ISC	In Situ Containment
IST	In Situ Treatment
LMWPAH	Low Molecular Weight Polycyclic Aromatic Hydrocarbon
LOE	Line of Evidence
MDL	Method Detection Limit
MNA	Monitored Natural Attenuation
MNR	Monitored Natural Recovery
NAS	Naval Air Station
NAVFAC	Naval Facilities Engineering Command
NCP	National Contingency Plan

NFA	No Further Action
NOM	Natural Organic Matter
NPL	National Priority List
NRC	National Research Council
OC	Organic Carbon
ONR	Office of Naval Research
OU	Operable Unit
PAH	Polycyclic Aromatic Hydrocarbon
Pb	Lead
PBT	Persistent Bioaccumulative Toxin
PCB	Polychlorinated Biphenyl
PEL	Probable Effects Level
PHC	Polychlorinated Hydrocarbon Compound
PRP	Potential Responsible Party
R&D	Research and Development
RAGS	Risk Assessment Guidance for Superfund
RAO	Remedial Action Objective
RPM	Remedial Project Manager
RI/FS	Remedial Investigation/Feasibility Study
SEM	Scanning Electron Micrograph
SETAC	Society of Environmental Toxicology and Chemistry
SITE	Superfund Innovative Technology Evaluation
SOP	Standard Operating Procedure
SPL	Seaplane Lagoon, Alameda Point (formerly NAS Alameda)
SQG	Sediment Quality Guideline
SRA	Screening Risk Assessment
tDDT	Sum of Dichlorodiphenyltrichloroethane and its degradation products (Dichlorodiphenyltrichloroethylene and Dichlorodiphenyldichloroethane)
TEL	Threshold Effects Level
TOC	Total Organic Carbon
tPAH	Total Polycyclic Aromatic Hydrocarbons
tPCB	Total Polychlorinated Biphenyl
TPH	Total Petroleum Hydrocarbons
TRV	Toxicity Reference Value
U.S. EPA	United States Environmental Protection Agency
VOA	Volatile Organic Analyte
WOE	Weight of Evidence
XRF	X-ray Fluorescence Spectrometry
Zn	Zinc

1. INTRODUCTION TO CONTAMINATED SEDIMENT ISSUES

1.1 MAGNITUDE OF THE PROBLEM

Sediments are the ultimate receptors of contaminants in effluent from urban, agricultural, industrial and recreational activities. Many sites have some level of contamination from anthropogenic sources. As sediment sites fall under increasing scrutiny, the number of sites that will need ecological risk assessment, and potentially, management, will probably increase. Determining the magnitude, nationally, of sediment problems can be difficult for a many reasons. Sediment sites are often not separated from other sites in organizational environmental databases, and these environmental data are often kept in different places, depending on the funding source, regulatory structure, the potentially responsible party (PRP) and site definition (e.g., construction, dredging, hotspot, National Priority List (NPL), etc.). Data searches also often fail because the term "sediment" has many definitions, depending on the user (e.g., sludge, soil, aquifer material, bottom sediments). Because sediment sites are usually on larger, industrial rivers and coastal areas, the extent of data coverage is limited. Most national inventories and surveys on the status of contaminated sediments¹ provide insight into only the edge of the problem. They report contaminants at the sediment surface, which are immediately available to benthic organisms, but little information exists to predict the three-dimensional extent of contaminant plumes, making even order of magnitude estimates of volumes and removal, containment, or treatment costs, tenuous.

Despite these complexities, a recent United States Environmental Protection Agency (U.S. EPA) report (U.S. EPA, 1998) identified 96 watersheds in the United States as having areas of probable concern for sediment contamination. For the U.S. Navy alone, it is estimated that contaminated sediment sites cleanup costs will be >\$500 M, possibly much higher. There are 110 facilities with identified sediment contamination, and 48 facilities with high relative risk, according to the Naval Facilities Engineering Command (NAVFAC) Normalization of Data system (NORM) database. Principal contaminants are metals, volatile organic analytes (VOAs), pesticides, polycyclic aromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs), often in mixtures.

Unless in-place management technologies gain acceptance, contaminated sediments will be removed, and then contained or treated. Despite current uncertainties about the risks and benefits of such an approach, the costs can be prohibitive, draining cleanup budgets. Estimated costs for such presumptive remedies will cost billions of dollars for the U. S. Navy alone (e.g., >\$100M for 110 acres at Naval Air Station (NAS) Alameda, Seaplane Lagoon; >\$200M for 1 M yd² at Long Beach Naval Complex). Nationally, the costs are also enormous. Given volumes of sediment potentially involved nationally and a median cost of remedial dredging of \$250/yd², one organization³ has estimated the cost to remove such sediments nationally as in excess of \$5 trillion. To manage these costs, contaminated sediment sites should be assessed, ranked, ranked, and prioritized, and cost-effective management strategies developed. The management process should seek to balance two parallel goals:

¹ e.g., <http://www.epa.gov/OST/cs/congress.html>

² Chief of Naval Operations (CNO). 1999. "Navy Policy for Conducting Ecological Risk Assessments," Ser N453E9U595355, Washington, DC.

³ Sediment Management Work Group. 1999. "Contaminated Sediment Management Technical Papers," <http://www.smwg.org/index.htm>

(1) minimizing contaminant risk to the environment and human health, and (2) minimizing cost (National Research Council [NRC], 1997).

1.2 DEFINITION OF TERMS

For clarity, a few terms will be defined because they can have different meanings depending on the background of the practitioner using them. The U.S. EPA defines contaminated sediments as “soils, sand and organic matter or minerals that accumulate on the bottom of a water body and contain toxic or hazardous materials that may adversely affect human health or the environment” (U.S. EPA, 1998). This definition makes no statement about the mechanism of contamination. Thus, while many sediments are contaminated as the result of anthropogenic activity, sediments can also be defined as contaminated even if contaminants exist due to natural processes. In this report, sediment assessment is defined as the process used to characterize sediment for a given purpose (e.g., evaluations for risks to environmental health, dredged disposal, land farming, habitat construction, etc.). Sediment management is defined as the process of making decisions and taking actions on sediments, considering a wide range of factors. Sediment management strategies or options can be defined as the range of actions that can be taken once risks have been assessed and risk managers have balanced those risks against various objectives and goals. These actions range from no action (either because risks do not exist or are not controllable) or institutional controls to more aggressive containments, treatments, or removal actions. Another important term used is Conceptual Site Model (CSM, e.g., American Society for Testing and Materials [ASTM], 1995; Apitz et al., 2002; 2005a). CSM can be defined as a three-dimensional description (either qualitative or quantitative or a mixture of both) of a site and its environment, which defines what is known (or suspected) about the contaminant source area(s) and physical, chemical, and biological processes that affect contaminant transport from the source(s) through environmental media to potential environmental receptors. Recognized as an important communication tool to facilitate stakeholder discussions and the decision-making process, CSMs are being used with greater frequency by state and federal agencies in the U.S. to aid in making sediment assessments a more focused effort, requiring only those data necessary to meet the goal(s) of the assessment strategy and objectives⁴ (Wenning and Ingersoll, 2002). The CSM should be continuously evaluated and refined as data become available, and, as the level of uncertainty associated with the CSM decreases, it should help identify data gaps and target additional investigations.

1.3 UNIQUENESS AND COMPLEXITY OF SEDIMENT SYSTEMS

Sediment investigations have many unique features that make them more difficult to manage than soil or terrestrial investigations. They integrate contaminant input from multiple sources within a watershed, creating difficulties in tracking sources of contamination. This integration also leads to ubiquitous, regional “background” levels of anthropogenic contaminants that are difficult to separate from site-specific sources. For the same reason, multiple contaminants (or chemicals or constituents) of potential concern (COPCs) impact sediments much more often than soils, making risk and management decisions complex. The hydrodynamics and geochemistry of sediment systems are also quite different than those of soil systems. While soils and groundwaters are often geographically removed from the receptors to be protected, sediments are in direct contact with the benthic community, near the base of

⁴ U.S. EPA. 2001. “Draft Report on the Incidence and Severity of Sediment Contamination in Surface Waters of the United States, National Sediment Quality Survey,” EPA-823-F-01-031, Washington, DC.

the aquatic food chain. Thus, remedial strategies can directly impact sensitive biota, and cleanup targets can be orders of magnitude lower than those in most soil sites, pushing the limits of assessment and cleanup technologies and increasing costs significantly over what may be needed for soils.

Because of these complexities, effectively managing contaminated sediments must be highly interdisciplinary. Chemistry, biology, ecology, hydrodynamics, and engineering must be considered and balanced. Good science alone does not yield good management—science must be linked with regulatory framework, politics, engineering, economics, public relations, and policy (site owner, federal and regional). While most soil cleanups are based on human health risk assessments, most sediment studies begin with ecological risk assessments. Sediments are subject to a multitude of regulatory criteria, from local to national and international. According to NRC (1997), “The mechanisms of the regulatory process in a given situation depend on where the sediments are located; where they will be placed; the nature and extent of the contamination; and whether the purpose of removing or manipulating the sediment is navigation dredging, environmental cleanup, site development or waste management.” As a result, multiple regulators or stakeholders may have different goals, cleanup criteria, or contaminants of concern, which drive their part of a site management decision.

Nationally, sediment management issues are highly politicized and newsworthy. Not surprisingly, given the complex environmental issues and the enormous potential costs in some regions, the decision process can be very adversarial. On the other hand, in other regions, sediment sites are managed with few problems. Despite this inconsistency, a consistent approach is not generally applied to sediments at different sites (with some notable exceptions). Approaches to contaminated sediments are in flux. Less than a decade ago, regulators (and most potentially responsible parties [PRPs]) thought that removal and treatment of contaminated sediments would be the remedy of choice; therefore, most sediment-related research and development (R&D) pursued technologies to support such an approach. However, based on potential volumes and projected treatment costs, estimated potential costs of the indiscriminate use of such an approach nationally are prohibitive. Thus, many (though not all) groups predict or advocate that large volumes of contaminated sediments will be managed in place. Clearly, the critical issue is how to determine what volumes of sediment actually require management, and for those that do, what is the most cost-effective but responsible approach. Large gaps in our knowledge of the fate of contaminants in place and the effects of in place and ex situ remedial strategies must be filled if management strategies are to be compared and chosen wisely.

1.4 THE NEED FOR SITE-SPECIFIC DATA IN SEDIMENT MANAGEMENT

The U.S. Navy, the U.S. EPA, and others are developing extensive sediment policy and guidance. Though various national and international sediment assessment and management frameworks, matrices, and flowcharts have existed for decades, sediment management remains complex and contentious for many reasons. First, our scientific understanding of the fundamental processes that control contaminant fate and behavior, from the simplest level such as contaminant/sediment/porewater interactions to the highest levels, such as ecosystem impact, is inadequate. The literature is rife with attempts to model contaminant behavior (e.g., flux, toxicity, or bioaccumulation) based on simple assumptions about specific sediment characteristics. In general, these attempts to find controlling parameters succeed for single sites, but do not extrapolate across disparate sites—contaminants behave differently in different environments (Chadwick et al., 2002; Rockne et al., 2002). Given this complexity, it

is impossible to predict the absolute risk of a given mix of anthropogenic contaminants on an ecosystem or human health without extensive site-specific analyses. The methodologies used to infer these processes in site assessments (e.g., sediment quality guidelines [SQGs], toxicity assays, and food chain models) are based on many assumptions and simplifications. For all but the simplest sites, anthropogenic contaminants can behave in sediments in complex and unpredictable ways, resulting in exceptions to the simple “rules of thumb” used to develop flowcharts, criteria, and guidelines. Thus, to make informed, effective sediment management decisions, site managers must use site-specific information, consider multiple lines of evidence, and communicate and negotiate using the best data available.

However, while resolving these uncertainties, it is critical that we proceed with the best practices available to assess, rank, prioritize, and begin to manage contaminated sediments. As NRC (2001) stated in their report on the management of PCB-contaminated sediments, “Management decisions must be made, even if information is imperfect.” Site assessment and ecological risk assessment (ERA) provide the best possible data on what the risks are at a given site in absolute and relative terms. The risk managers (in the form of RPMs, regulators, stakeholders, and their support personnel) evaluate if that risk is acceptable and/or manageable. Contaminated sediment management is complex and multivariate, involving a careful balance of science, politics, and economics. As is true for most complex issues, a single correct way to address a problem does not exist, but depends on the ecological, political, and economic goals of all interested parties. In such complex systems, “truth” is non-existent, just an attempt to balance knowledge, uncertainty, and policy to make decisions that are negotiated with the information available. Factors in sediment assessment and management are so varied that no guidance or flowchart can anticipate every permutation. Thus, it is always necessary to (1) use professional judgment, and (2) to negotiate. Site-specific data accomplish this goal most effectively. Understanding of site-specific contaminant/sediment geochemical interactions and using these data in decision-making and negotiation are among the many tools that allow the U.S. Navy to address these issues more effectively.

In this introduction, aspects of assessing and managing sediments are discussed, as well as sediment management goals that drive (or should drive) these goals. Data on contaminant/sediment biogeochemical characteristics help guide, define, negotiate, and comply with these goals. In most cases, this report is consistent with the recently published U.S. EPA “Principles for Managing Contaminated Sediment Risks at Hazardous Waste Sites” (U.S. EPA, 2002), and sections of this guidance should help risk assessors and managers manage sediments in line with these principles. As with every issue that is complex in regulatory and technical terms, all steps of the process should be designed and conducted in close collaboration and communication with all parties. This report highlights many successful aspects of contaminated sediment assessment and management. It also provides site owners with examples of how to use site-specific data to compare site, background, and regional sediment signatures to address risk, determine responsibility for inputs, rank sites, and prioritize management; to help bridge the gap between remedial investigations and feasibility studies in a meaningful way; and to provide site owners with the tools to rapidly determine what sediment management approaches are feasible for contaminated sediments at their sites—and to use site data to evaluate, communicate, and negotiate management choices. This report also highlights some major uses for data on contaminant/sediment geochemical interactions in the assessment and management of contaminated sediments. It is not an exhaustive review of all potentialities, yet it does provide many examples, case studies, and SOPs that should aid RPMs, risk assessors, and managers in using site data to evaluate, negotiate, and select management strategies (**Tables 1 and 2**). *While these examples and case studies are largely*

derived from data at actual sites, data or approaches have been modified to enhance their illustrative use. The case studies are intended to illustrate the use of data for a particular purpose, and are not necessarily relevant to any particular site, and should not be used in that context.

Table 1. Sediment characterization case studies.

CS#	Title	Section	Scenario	Data Set	COPCs
1	Application of Various SQGs	2.4	Impact of applying different SQGS in evaluating risk or delineating OUS	Site 3	PCBs, Cu, Zn, Pb
2	Separation of Site and Background Levels	2.6	Use of morphological Lines-of-Evidence to separate site and background levels	Site 4	Cu
3	Metals Background	3.2.1	Background considerations for metal COPCs (cross plots)	Site 1	Cu, Pb
3a	Metals Background addendum	3.2.1	Lines-of-Evidence (flux, grain size)	Site 1	Cu
4	Organics Background	3.2.1	Background considerations for organic COPCs (HQ, cross plots, signatures)	Site 2	PCBs
5	Detection Frequency	3.2.2	Detection frequency of COPCs (HQ, OU division)	Site 2	Pb, Zn, Cd, Cr
6	Metals LOE	3.4	Metals COPC Lines-of-Evidence (flux, bioaccumulation, size fraction)	Site 2	Pb
7	Organics LOE	3.4	PAH COPC Lines-of-Evidence (size fraction distribution, signatures)	Site 2	PAH
8	Interpretation of Contaminant Mass Distribution	4.1	Evaluation of organic mass distribution to address management goals	Site 2	PAHs, PCBs, DDT
9	Mixing Scenarios	4.3	Metals: Erosional events (depth profiles, OU, mixing)	Site 3	Cu
10	Monitored Natural Recovery	4.3	PAHs: Biodegradation of PAHs (before and after)	Site 2	PAH, Pb, Zn, Cd, Cr
11	Pretreatment Cost Evaluation	4.6	Cost implications of size separation pretreatment	Site 3	Cu

Table 2. Sediment characterization examples.

Ex#	Title	Section	Scenario	Data Set	COPCs
1	Impact of processing data	2.3	Differences in data processing and interpretation: PB results contoured (1) without bias, (2) by ER-L and (3) by ER-M	Site 2	Pb
2	Selection of Appropriate Sediment Benchmarks	2.4	Concentrations of organic contaminants in OU sediments compared to potential benchmark values	Site 2	Organics
3	Use of Equivalent Datasets	2.5	Risk evaluation and site prioritization based upon inappropriate data comparisons	Site 2	Cr
4	Average Crustal Abundance	2.5	Comparison of various sediment quality benchmarks to the average crustal abundance for seven metals	General	Metals
5	Total PAH Summations	2.5	Total PAH (tPAH) summations of different data sets from the same site compared to ER-L and ER-M benchmarks	Site 2	PAHs
6	Method Detection Limits	2.5	Variations in contaminant distribution contours for data reported as sums of analytes	Site 2	Organics

Because countless variables must be considered in a sediment assessment and management decision, it is impossible to write a guide or flowchart to anticipate every scenario, or to provide an acceptable “black-box” decision matrix. What complicates sediment management are the intricate ways that contaminants can behave, in short, contaminant/sediment geo-chemical interactions. Essentially, this project has endeavored to demonstrate how an understanding and intelligent use of data on these interactions can aid in cost-effective sediment management. These issues were largely ignored (except by rare and expensive experts) a few years ago, and now they are routinely addressed, allowing RPMs to be much more “in control” at their sites.

1.5 CATEGORIES OF SEDIMENT MANAGEMENT

While every rule has exceptions, the field of contaminated sediment management can be divided into two general categories, largely defined by the purpose for which they are examined. The first, construction or navigational dredging generally involves the assessment and removal of large volumes of sediment. In many cases, these sediments have lower contaminant levels, or contaminants reside in areas considered of lower ecological significance than “hotspot” sediments and, thus, they would not generally be the subjects of immediate environmental investigation if they were not the target of a dredging operation. Of course, in areas with high levels of historical contamination, or sites with significant ongoing

contaminant input, these sites may have high levels of contamination that cannot be managed until sources are controlled or resources are available. Because removal is a given in this aspect of sediment management (unless environmental or economical problems bar it), assessment addresses the risks of resuspension through dredging, disposal, beneficial uses, and/or treatment options. While some information in this report may assist in a standard assessment where removal is a given (i.e., for construction dredging, etc.), in general, guidance and policy are clearly laid out for this situation, and this category of sediment management is not the focus of this report.

The second type of sediment management, hotspot or environmental cleanup of contaminated sediments, generally addresses smaller volumes of sediment, though there are notable exceptions. The sediments addressed for this purpose may have much higher contaminant levels than sediments managed for navigation and construction dredging; they may reside in areas of ecological significance or they may contain substances of particular concern (e.g., bioaccumulative substances), prompting immediate investigation and/or management. These sediments become the target of investigation when a spill, survey, toxic effect, or historical record flags them as potentially posing a risk to human health, fisheries, or the environment. For the U.S. Navy, programs such as Base Realignment and Closure (BRAC), etc., can also cause a site to be targeted for examination. Assessment of such sediments can focus on absolute and relative risk, as well as risks of in-place versus removal options.

Primarily because of the large influence of the dredging community on sediment assessment and management in North America (Power and Chapman, 1992), until recently, most sediment management approaches and research focused primarily on *ex situ* sediment treatment and disposal options rather than on in-place management and risks. Essentially, one can argue that the tools developed for environmental assessment and management of sediments were derived from dredging and disposal. However, due to the large volumes of sediment managed in recent years, many (though not all) groups predict or advocate that large volumes of contaminated sediment will be managed in place (unless dredging is the driver), largely because of the potential costs involved. Thus, sediment frameworks and research are evolving to match these specific objectives, leading to improved approaches for site assessment to delineate contamination and better use of site data to frame management decisions.

Many factors, scientific and non-scientific, must be addressed in sediment assessment and management. Science factors, which define and are guided by the CSM, include sediment type (grain size, percent, and quality organic carbon [OC], mineralogy, etc.) receptors of concern, exposure routes, contaminant type(s), water type (marine, fresh, brackish), physical dynamics (deposition, erosion, tidal cycles, wave action), and the proportion of contaminated sediment to uncontaminated sediment. Non-science factors (which define and are guided by the management goals) include management objectives, regulatory framework, protection goals, public interest(s), resources (financial and technical), economic implications of any action, perceived risk, "cuteness coefficient" (whether or not charismatic animals are potentially at risk), and time factors. A summary of approaches for addressing many issues is in Apitz et al. (2002) and its references. This report addresses how data on sediment/contaminant geochemical signatures and interactions can be used to address many of these issues.

The U.S. Navy policy, regulatory frameworks, and technical communities that address these two sediment categories are separate, with little or ineffective interaction. Assumptions, methods, and frameworks designed to address one category may be inappropriate for the other. However, note that sediment characteristics remain the same regardless of the manage-

ment goals interested parties may apply to them, and that the only real differences lie in the evaluation and management, not in the sediments themselves.

1.6 SEDIMENT MANAGEMENT STRATEGIES OR OPTIONS

Sediment management strategies fall into five broad categories that are selected based on an evaluation of site specific risks and goals: (1) no action, which is only appropriately applied if it is determined that sediments pose no risk; (2) monitored natural recovery, based on the assumption that while sediments pose some risk, it is low enough that natural processes can reduce risk over time in a reasonably safe manner; (3) in situ containment, in which sediment contaminants are in some manner isolated from target organisms, though the sediments are left in place; (4) in situ treatment; and (5) dredging or excavation (followed by ex situ treatment, disposal, and/or reuse). The information required to evaluate or compare each option is fundamentally different, and any assessment should be designed to evaluate and support management goals and potential remedial options. U.S. EPA guidelines suggest that "All remedies that may potentially meet the removal or remedial action objectives... should be evaluated prior to selecting the remedy" (U.S. EPA OSWER, 2002), careful planning is necessary to ensure that sampling and analysis plans are designed to address these disparate needs in a meaningful and comparable way.

1.7 TYPES OF SEDIMENT ASSESSMENT

Sediment assessment frameworks can exist on a continuum, from specific decision trees designed to select dredge disposal options to custom ERA designed to assess risk and select an environmental management strategy. As with sediment management, a review of sediment assessment frameworks from jurisdictions active in sediment management throughout the world (Apitz and Power, 2002) revealed that when organized by their management objectives, two main categories emerge: dredged disposal and environmental assessment and management (e.g., general assessment of environmental quality and more focused assessment of contaminated sites with sediment issues). In addition to environmental assessment/management guidance tailored for sediments, which is very often risk-based, many generic ecological risk frameworks are applied to sediment issues on a site-specific basis.

Due to their narrow focus, frameworks designed for assessing dredge disposal options are relatively inflexible, but are relatively simple to use because they provide specific guidance. The experience level required to conduct such an assessment can be less than that required for sediment assessments for other purposes. In contrast, sediment assessment frameworks designed to support environmental management strategies can be highly flexible and quite complex. As a result, they tend to have elaborate guidance or provide general, flexible guidance. In either case, they usually require a high level of experience to perform successfully, particularly when they are linked to sediment remediation planning.

1.8 RISK

An important element of a sediment assessment process is the application of the ERA framework and approach that assesses the probability that exposure to one or more stressors (i.e., contaminants) will lead to adverse ecological effects (U.S. EPA, 1997). The assessment provides information relevant to the management decision-making process. Ideally, ERAs should be scientifically based, defensible, cost-effective, and protective of human health and

the environment⁵. The complexity and heterogeneity of aquatic ecosystems often hinders the collection of data necessary to support cost-effective decisions at sediment sites. Detailed site investigations require extensive sampling and subsequent laboratory analyses for metal and organic contaminants. This approach can be prohibitively costly, slow, and labor-intensive if not conducted in a tiered fashion. As such, the ERA framework will be useful to designing effective data collection plans and the use of that data in the decision-making process.

A “classical” ecologist's definition of ecological risk assessment (ecorisk) is the product of the magnitude of the adverse ecological effects (hazard) and the probability of adverse ecological risk (exposure). Simply, even the most toxic material does not pose risk if no exposure pathway to an organism exists, but if an organism will probably be exposed to toxics frequently or for an extended time, even relatively less-toxic materials can pose significant risk. However, many types of risk exist, and what is evaluated depends on the goals and the CSM. A few examples are absolute ecorisk (i.e., “Does sediment x put species y at risk?”), site-specific risk (e.g., “What is the risk of sediment x relative to regional or background risk?”), manageable risk (i.e., “Can this risk be controlled?”), and management option risk (e.g., “What is the risk of leaving sediments in place versus disturbing them?”). Data on sediment/contaminant signatures and interactions can be used to ensure that assessment and management frameworks (which are essentially risk-based) can address absolute risk to a specific target organism or community, to rank sediments within a region, to compare site-specific and regional or background risk, or to select and evaluate management strategies.

1.9 CRITICAL FACTORS IN SEDIMENT ASSESSMENT AND MANAGEMENT

1.9.1 Sediment Quality Guidelines

An important tool in many sediment assessment frameworks is the use of sediment quality guidelines (SQGs), also known as action levels, criteria, standards, trigger values, or screening values. “Sediment numbers” have been developed in many jurisdictions for both categories of sediment management described in this report (compilations in Environmental Consultants (EVS), 1998; Chapman, Allard, and Vigers, 1999). In most frameworks reviewed, they are not designed for use as disposal or cleanup criteria. However, sediment guidelines and their derivation methods are still controversial, and their appropriateness should be carefully evaluated in terms of site management goals, study questions, and the CSM. Two recent documents that address the use of SQGs and weight-of-evidence frameworks are Chapman et al. (2001) and Batley et al. (2002). A recent Pellston workshop addressed this issue. A summary of workshop conclusions is available at the following URL: <http://www.setac.org/pubsws.html>. One major conclusion was that site-specific information and multiple lines of evidence are required to make most management decisions. In summary, while SQGs are useful for flagging potentially toxic contaminant levels in sediments, and can thus indicate which sediments may be of no concern and those that merit a closer look, site-specific considerations and biological analyses should be used to develop remedial goals at a site. This report addresses many of these site-specific considerations and their application (see **Section 2.4 for a more detailed discussion**).

⁵ Chief of Naval Operations (CNO). 1999. “Navy Policy for Conducting Ecological Risk Assessments,” Ser N453E/9U595355, Washington, DC.

1.9.2 References, Controls, and Background Levels

An important issue that must be addressed in a sediment management framework is how one identifies reference sites and background contaminant levels. Reference areas can be used to make comparisons among biological, chemical, or physical sediment data that might be collected from an area under study. Lack of appropriate criteria for selecting the reference areas may result in an inappropriate location selection and inappropriate sediment management action. Identification of the reference site may depend on the remedial goals and options, historical and existing conditions at the site, and the critical physical, chemical, and biological parameters evaluated. An important part of defining reference conditions is sediment biogeochemistry.

While absolute concentrations of contaminants in sediments are an important part of assessing site sediments, these concentrations do not provide a full picture of what is happening at the site. Organic and inorganic contaminants can exist in a region at background, ambient, or natural levels because they have natural sources or entire regions in urbanized, industrialized, and other areas that are exposed to ubiquitous levels of anthropogenic input. In many cases, because such contaminants tend to associate with fine-grained sediments, a general regional tendency is to have a “mixing curve” of contaminated fines, and relatively uncontaminated coarse-grained sediments. Often, either ambient contaminant levels or background natural levels, or a combination of both, can be separated from site-specific levels by normalizing to or plotting against sediment characteristics that tend to indicate natural metal-rich particles (e.g., Fe, Al) or fine-grained particles (e.g., Fe, Al, %fines, %OC). While ambient or background levels of contaminants can be bioavailable, and may cause ecological impact, they are almost impossible to manage on a site-specific basis—cost and logistics make it improbable that an entire region will be remediated, and if specific sites are remediated to below ambient levels, those sediments will probably be subject to recontamination by background sediments. Thus, it is important at a given site to examine contaminant distribution relative to regional, ambient, or background levels, and to select reference sites with care (Apitz et al., 2002, and 2005a and b). This report discusses how data on sediment/contaminant geochemical signatures and interactions can be used to address these issues (see **Section 2.6 for a more detailed discussion**).

1.9.3 Pathways of Contaminant Transport

Many dynamic pathways may contribute to contaminant transport and exposure at contaminated sediment sites. These pathways include the effects of bed transport, bioturbation, diffusion and advection, resuspension and deposition, and transformation and degradation. The relative rates of these processes help define the potential risk of in-place sediments, pathways of exposure that must be controlled, and potentially, mechanisms of natural recovery of the sediment. A risk assessment that considers in-place management options must address all these factors. An understanding of the relative importance of these processes at sites will focus site conceptual models and help risk managers balance these processes to minimize risk and, ideally, optimize recovery (Apitz and Chadwick, 1999; 2001). Such an evaluation should provide sufficient information to support decisions about which sediments can responsibly be managed in place, how aggressively they should be monitored or contained, or whether they should be removed and managed ex situ. Sediment containment and disposal options that can be considered under appropriate circumstances include landfills, confined disposal facilities, in-place natural recovery, contained aquatic disposal, in situ capping, and deep-ocean disposal. To evaluate these, sediment quality and risk must be compared to that of target environments. If removal is a given for dredging purposes, in-place risk is less

important than it would be for a hotspot site (although it might need mitigation), and assessments may not focus on it. If removal is under evaluation, then risks of removal, transport, treatment, and/or disposal in various environments must be evaluated.

1.9.4 Keys To Successful Sediment Management

Some keys to success in a sediment investigation (one in which data collection and assessment are designed to technically support management decisions that fulfill environmental, economic, and political goals) are as follows: (1) design sediment assessment to match short-listed sediment management options; (2) develop a remedial investigation (RI)/feasibility study (FS) as a series of building blocks held together by an overall tiered framework; (3) ensure that decision-making is transparent and somewhat standardized, but flexible enough to meet national/regional goals (i.e., which is in line with current organizational, regional, national, and international agreements and guidance); (4) build natural and regional background concentrations, reference sites, and site-specific bioavailability considerations into assessment; (5) wherever possible, ensure that source control is a primary requirement before other management strategies are applied (this may not always be possible on a watershed-wide basis); and (6) while sediment guidelines have an important role, they should not be used as pass/fail values—but as triggers for further investigation. Site-specific thresholds are much more useful.

Because sediments are highly mobile and do not respect property, national, or ecological boundaries, wherever possible, assessment and management strategies should be applied on a watershed or catchment basis, with sediments that are hydrologically linked, assessed, ranked, prioritized, and managed on a regional basis. Implicit in such an approach are source control and resource-sharing issues that will require inter-organizational cooperation. While the focus and driver of a study may be a specific site, it will ultimately be more cost-effective to consider together, at least at some minimal level, the entire lifecycle of sediments and their associated contaminants within a catchment, from source to ultimate sink. Therefore, sediment management strategies should be considered in the wider context of sustainable sediment management from beginning to end. To ensure that the sediment studies will be appropriate for a particular set of management goals, it is important that any sediment assessment and management study developed is consistent with all regulatory frameworks that may impact it. Lastly, because sediments can preserve contaminants long after sources have been controlled, and can ultimately be a source of those contaminants to the environment, sediment management is an important part of meeting ecological goals, and these goals may thus affect the management objectives of the U.S. Navy throughout their activities.

It is important that early in sediment RI/FS design that all interested parties define their management goals for sediment and that these goals (along with regulatory and U.S. Navy policy) drive investigation design, leading to efficient sediment assessment and management. A review of worldwide sediment assessment and management frameworks and case studies makes it clear that any study not built around a CSM or not focused on or defined by management goals runs the risk of being open-ended, iterative, expensive, and inconclusive. In complex, multivariate natural systems, no amount of data can provide an answer unless a question has been defined. It will thus be important for site managers and stakeholders to review and define regional sediment practices, ecological priorities, and objectives (at local and at higher levels) before designing sediment assessment and management strategies and the tools used to support them.

2. MAXIMIZING DATA USE FOR CONTAMINATED SEDIMENT ASSESSMENT AND MANAGEMENT

Frequently, original site assessment data are collected without input from the eventual modelers, decision-makers, and risk managers on data needs. Because sediment risk assessments have often started with no clear idea of where along the continuum site management would end, data were often collected in an iterative manner. A minor extra investment to ensure that samples and data collected will serve the needs and priorities of multiple users or stakeholders can ensure broader use of data and help prevent multiple sampling events, thus expediting site decisions at reduced cost. Once collected, it is critical that data are summarized and communicated to address the concerns and priorities of all stakeholders who will be part of the decision process (for examples of some approaches, see Kirtay, Leather, and Apitz, 2000; Apitz, 1998; Apitz, 1999a and b). The following subsections provide several approaches to sediment data use that can help streamline the sediment assessment and management process.

2.1 NEGOTIATE OBJECTIVES, DECISION CRITERIA, AND SITE CONCEPTUAL MODELS UP FRONT

Data have frequently been collected without input or consensus from the full suite of stakeholders. A stumbling block to efficient data use has been the inability to compile and integrate or synthesize data, especially from multiple sources, in a uniform or mutually agreeable manner. Another problem at times has been a lack of openness in the process, resulting in distrust and extreme positions by some regulators, RPMs, and stakeholders. Unless these issues are resolved up front, progress is improbable at a site. One major observation of the National Research Council (1997) was that openness, communication, and buy-in by all parties early in the process led to successful case studies. This process can be difficult, given that different parties may have vastly different decision drivers, but if costs are needlessly inflated by a failure to negotiate, all parties (barring, perhaps, cost-plus consultants) can lose. PRPs can spend countless millions assessing and re-assessing the sites, but in a world of limited budgets, this spending can also reduce the funds available for ultimate remedial actions, possibly reducing remedial effectiveness.

2.2 DO NOT GENERATE NEW DATA WHERE DATA EXIST

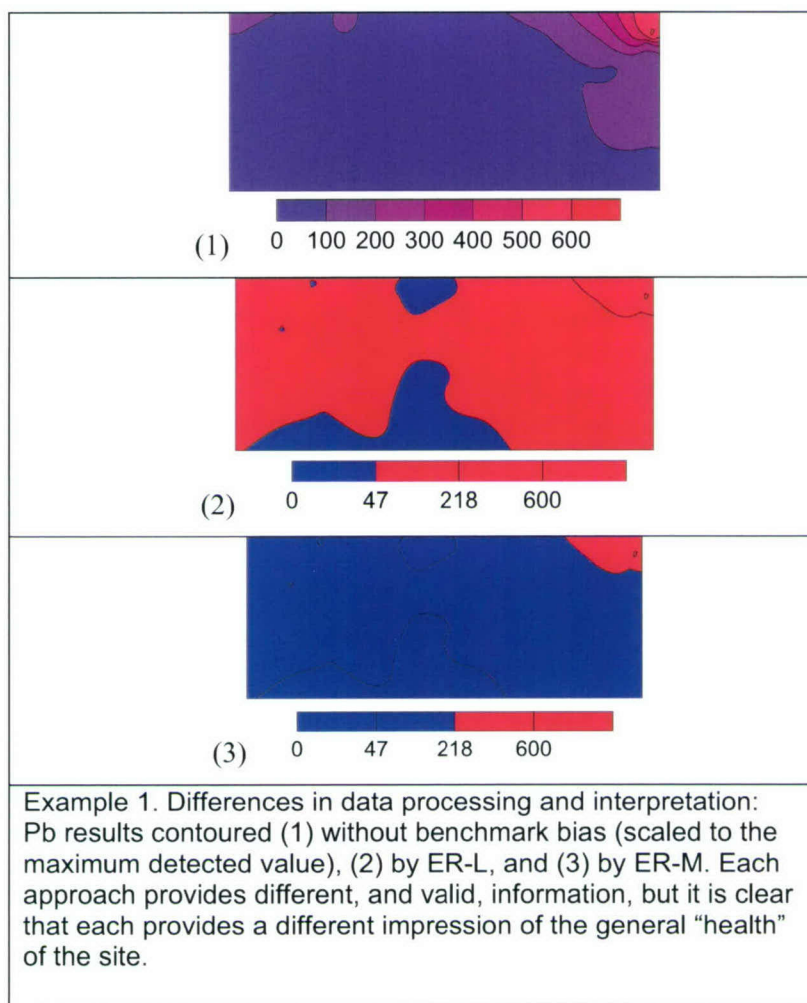
Personnel turnover (by RPMs, regulators, and contractors) often leads to a desire to start over, rather than to "mine" existing information or honor predecessors' commitments. This turnover can lead to costly, iterative studies. Some stakeholders have a tendency to fall into the "deep-pocket syndrome" in which PRPs are pressured to collect data that would otherwise not be available but have no relevance to the decision process. Unless such an approach is specifically and explicitly negotiated, or it is funded by complementary R&D dollars, data collections that do not clearly support the remedial investigation and feasibility study (RI/FS) are not justified. Examination of case studies reveals many cases in which sites were re-studied iteratively over decades. Though different regulatory and assessment frameworks have often been applied each time, little extra information has been gained from repeated analyses that could not have been gleaned by a careful re-analysis of existing data. While there are many reasons to seek more data at a site, a critical assessment should first be performed on currently available data. Any further sampling plans should satisfy criteria (which are essentially part of the DQO process; see <http://enviro.nfesc.navy.mil/erb/> for

documents and guidance on the DQO process in general): (1) Do these analyses fill existing data gaps? (2) Are these data relevant to decision criteria? (3) How will the data be used? (4) Have all stakeholders or decision-makers agreed on the need and use of these data?

2.3 STORE DATA IN UNPROCESSED FORM FOR FUTURE, UNANTICIPATED USE

While most site interpretation and negotiation will be based on highly processed data (i.e., graphs, statistical summaries, contour plots, etc.), it is important to also ensure that all data collected are available in a relatively unprocessed, preferably digital form. This form allows for the repeated use of data to address questions possibly unanticipated at its collection. For instance, while total PAH (tPAH) numbers are needed to compare to potential sediment quality criteria or benchmarks, the PAH fingerprints (the relative distribution of individual PAHs) can provide a significant amount of information on source, background, weathering patterns, potential toxicity, and the potential for natural attenuation. Thus, although generating tPAH numbers may be the primary purpose of an initial data collection, processing and storing the more detailed distribution information allows for more detailed analysis, if necessary, at a later date. The importance of this approach is demonstrated in several case studies and examples (see **Tables 1 and 2, Section 1.4**) where the same data were used in different forms for different purposes. Making neutral, unprocessed data available is an important part of data openness, which aids in good-faith negotiations. Potentially suspicious stakeholders may be much more willing to accept data as sufficient if they can access and manipulate it themselves with different approaches and assumptions. Generally, once data are mapped, contoured, or plotted, they have already been highly processed in ways that can be driven by the assumptions of the author. Simple factors such as the color choice in a contour, what benchmark values are normalized to, etc., can affect the way graphics look, and the message they convey.

Example 1 shows the impact of processing data. In the first plot, surface sediment Pb data are contoured in relative terms without being normalized to or put in terms of any benchmarks. Using two different benchmarks, Effects Range-Low (ER-L) and Effects Range-Median (ER-M), respectively, the same data are then contoured as color thresholds. By changing the assumptions or scales by which the data are plotted, the perceived area of concern changes drastically to potentially just one corner of the site. While the practice of using the range of detected values as a full-color scale has some validity, it causes even sites with only relatively low values to have apparent hotspots at whatever points top the scale. On the other hand, scaling to benchmarks, while flagging exceedances, can blur the distinctions between samples by distorting the scale—either to high or low values. Visual data presentation is a powerful tool for synthesizing and conveying information. However, because it does process data in a way that focuses on selected questions or objectives, it should also be made available in forms that allow others to evaluate it at other levels. If all stakeholders can access data and subject them to their own benchmarks, criteria, or assumptions, then communication and negotiation can be aided. In summary, critical data must be distilled for presentation to stakeholders, but still be transparent.

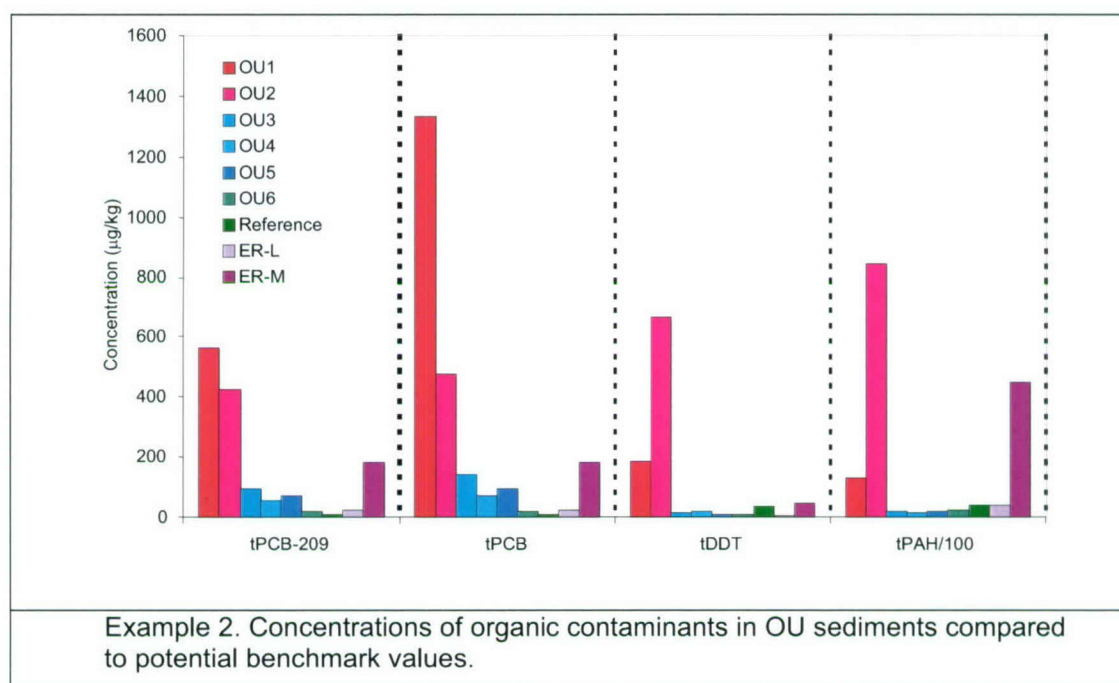


2.4 SELECT APPROPRIATE SEDIMENT BENCHMARKS

Whenever one looks at bulk chemical concentrations in sediments, it is important to compare them to some criterion or benchmark to put the values into perspective. However, a choice of appropriate benchmarks depends on a definition of the objectives of the work. If the objective is a determination of the potential risk of a contaminant of potential concern (COPC) in the sediments, one can compare bulk chemical values to levels that are expected to be toxic in sediments (e.g., ER-L, ER-M, Threshold Effects Level [TEL], Probable Effects Level [PEL], and Apparent Effects Thresholds [AETs]). Such values are often termed Sediment Quality Guidelines (SQGs). The basis, strengths, and weaknesses of SQGs were summarized in a recent Society of Environmental Toxicology and Chemistry (SETAC) workshop document (available at <http://www.setac.org/pubs/ws.html>). A recent paper (Chapman et al., 2001) addresses many of the challenges and complexities of this issue. If the objective is to determine whether, for a given COPC, the sediment examined differs from other comparable sediments, one can compare bulk chemical values to background, regional, or reference values. In **Example 2**, organic COPCs are compared to regional reference value, ER-L and ER-M. Operable Unit (OU) 2 exceeds all benchmarks for all classes of organic COPCs shown, and OU1 is also very high. This observation suggests that risk will probably

be not only absolute, but also site-specific, in these units for organic COPCs. The story for the other units is a bit different. For PAHs and tDDT, OUs 3 through 6 have levels below regional reference levels (as well as ER-L and ER-M), and thus do not present risk from those contaminants. PCBs in OUs 3 through 5, on the other hand, have levels below ER-M, but above ER-L and regional reference levels. Depending on management priorities, the elevated PCB levels in these OUs (relative to regional values) may cause concern, and may warrant further risk evaluation. Often, a combination of the above is useful if data may be used in more than one way. **Case Study 1** (Figures 1-1 through 1-3) demonstrates the impact of applying different criteria in evaluating risk or delineating OUs.

Within a regulatory program, the SQGs used are often clearly laid out or negotiated up front. If not specified by the regulatory structure, candidate SQGs could be selected and adapted to suit project objectives. Ultimately, the goal is to identify benchmark values that are relevant in regulatory and regional terms, but that are also as technically comparable to data collected within a project. While the benchmarks described above are useful as screening tools, it is important to remember that bulk sediment COPC concentrations alone are not enough to make risk decisions. If screening concentrations are exceeded, though, more detailed examination is probably warranted.



CASE STUDY 1: APPLICATION OF VARIOUS SQGS

At this site, Cu, Zn, Pb, and tPCB results were normalized to different sediment quality guidelines, including a site-specific bioaccumulation factor derived for PCBs. Cumulative frequency distributions were then plotted to identify natural break points in concentration, which may indicate different underlying populations or geographical areas. These values were used for developing spatial plots to aid in delineating potential strata. As shown below, depending on the decision criteria negotiated, very different volumes of sediment could be “flagged” as areas of concern. If PCBs are a major concern, and background values are used as the benchmark (in this case, defined as Ref85 values), a very large area may require aggressive management. On the other hand, ER-M and site-specific bioavailability models suggest much smaller areas requiring management.

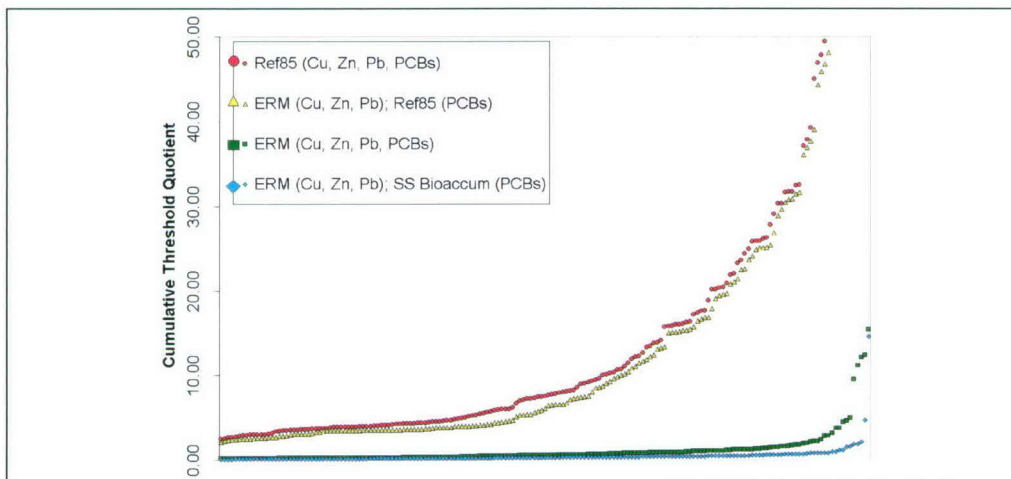


Figure 1-1. Cumulative threshold quotient for different sediment quality guidelines.

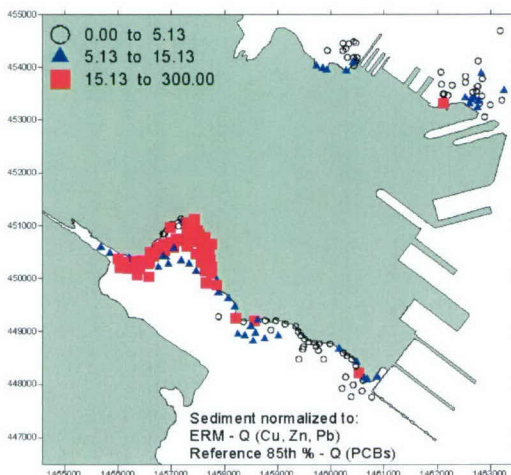


Figure 1-2. Reference 85th Percentile Quotient.

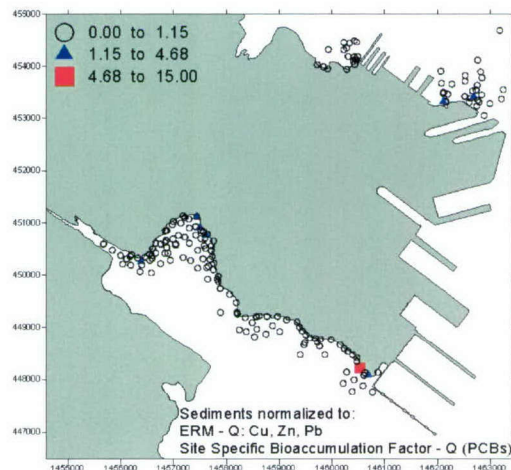


Figure 1-3. Site-Specific Quotient.

One approach that can be applied is to generate site-specific benchmark values based on site chemistry and bioassay results. Contaminant levels in sediments at a site can be compared with toxicity assays, bioaccumulation, or flux measurements in the same sediments. If correlations are observed, "acceptable" contaminant levels can be selected for the site based on these values. In the previous case study, a site-specific bioaccumulation factor for PCBs was derived. The details of this derivation are beyond the scope of this work.

2.5 INTEGRATE SITE AND REGIONAL DATA TO PUT SITES IN PERSPECTIVE

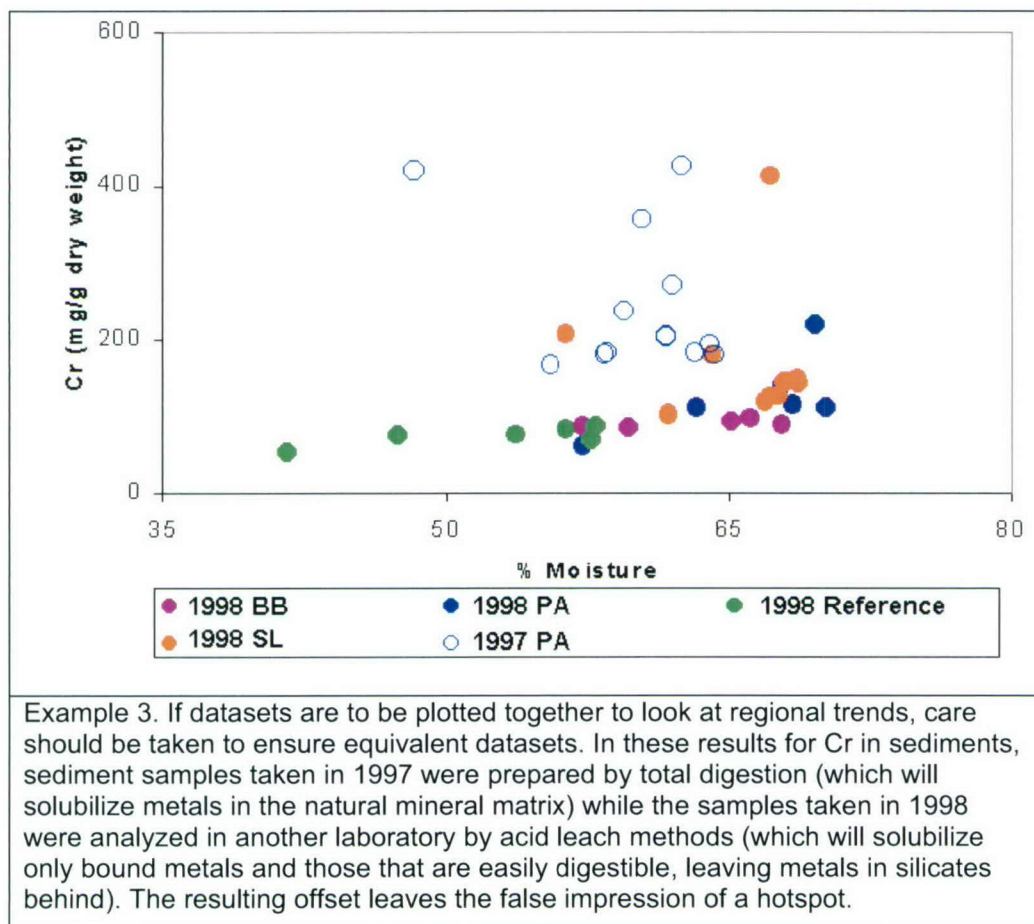
Most contaminated sediment sites exist in highly populated or industrialized areas. Because of the dynamic nature of sediment systems and the tendency of contaminants to associate with organic-rich, fine-grained sediments, entire regions may have some level of impact from anthropogenic compounds. Contaminated sediments may have originated at a remote location, and settled at the site of concern. Sediments may have some level of a COPC that originated near the site, some which came from remote sites, some at regional background levels, and some, for many chemicals, at natural background levels. Sediments with mixed contaminants may have a different mix of sources for each COPC. For these and other reasons, evaluating and managing individual sediment sites in a vacuum, while not putting them in terms of other impacted and background sites in the region, can be short-sighted and misleading. Within a region, regardless of PRP or site owner, it is useful to compare data on a site of concern with data available on other sites. This comparison allows the following: (1) an evaluation of potential contaminant sources, either historical or ongoing; (2) an evaluation of the relative severity of impact at multiple sites; and (3) an evaluation of site COPC levels relative to regional reference or background levels.

While a site under investigation is contaminated at lower levels than other sites in the region does not remove PRP responsibility to manage the site (if risk is established), information on the relative risks of sites in a region may help avoid many undesirable outcomes, including the following: (1) improper allocation of limited resources by cleaning up sites based on a schedule instead of relative risk (for a PRP with multiple sites in a region), (2) re-contamination of a cleaned site by adjacent sites left in place or managed later in a manner that allows dispersion, or (3) cleanup of sites not impacted at levels above regional background concentrations.

To achieve this goal, however, all samples, including those from reference sites, must be evaluated in the same manner as those from sites of concern. If site data are to be plotted together to examine regional trends, care should be taken to ensure equivalent data sets. Thus, all sites must be evaluated relative to the same set of benchmarks, and with comparable analytical methods. To achieve the latter, it is important to ensure that laboratories that performed analyses collected, analyzed, processed, and reported data in a comparable manner. The following paragraphs discuss some examples of potential pitfalls to comparison:

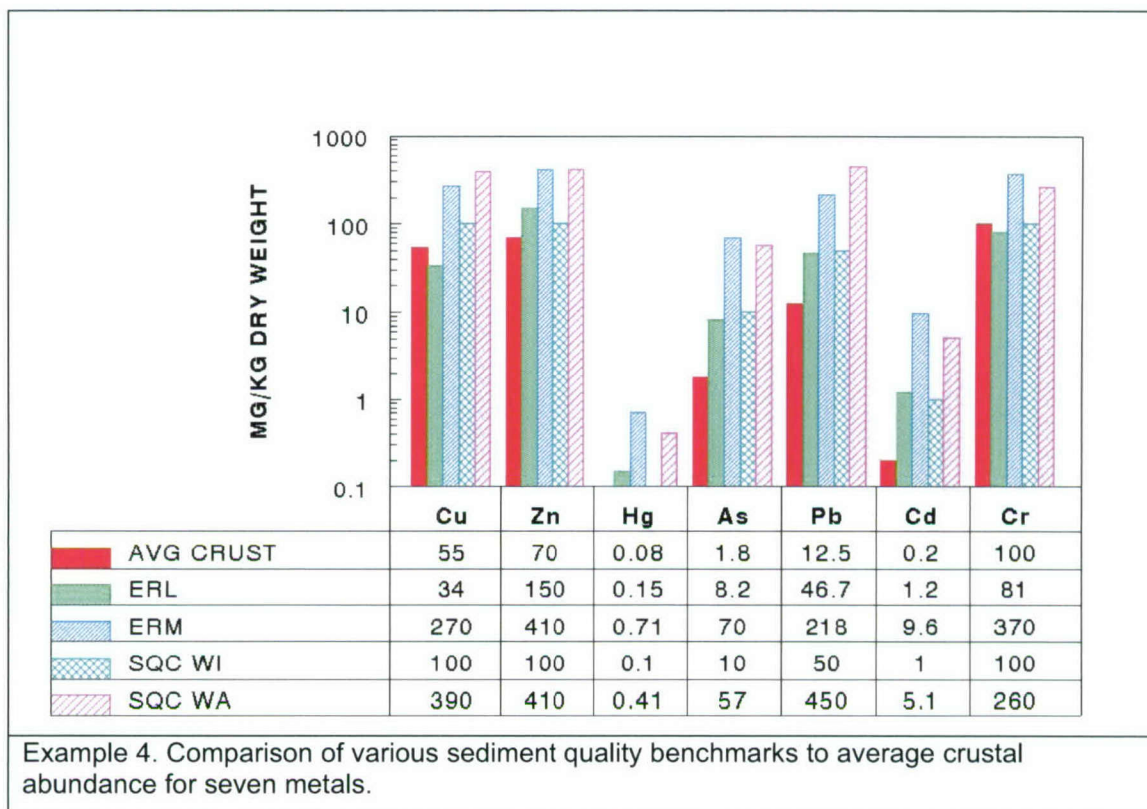
Metals can be analyzed in many ways (total, acid leachable, acid-volatile sulfides [AVS]/scanning electron micrograph [SEM], X-ray fluorescence spectrometry [XRF], etc.). Results from these different approaches are not directly comparable, and cannot be meaningfully contoured together. Attempts to do so for regional comparisons can result in "false hotspots." For instance, as in **Example 3**, if Cr is contoured in a region, with most sites reporting acid leachable Cr, and one site reporting Cr measured by total digestion, the latter site may have Cr that appears significantly higher than the other sites, but actually comes from the natural mineral matrices, and is thus not ecologically relevant. If sites are targeted or prioritized

based on such inappropriate comparisons, evaluations of relative risk, as well as site prioritization and identification of COPCs will be unsuccessful.



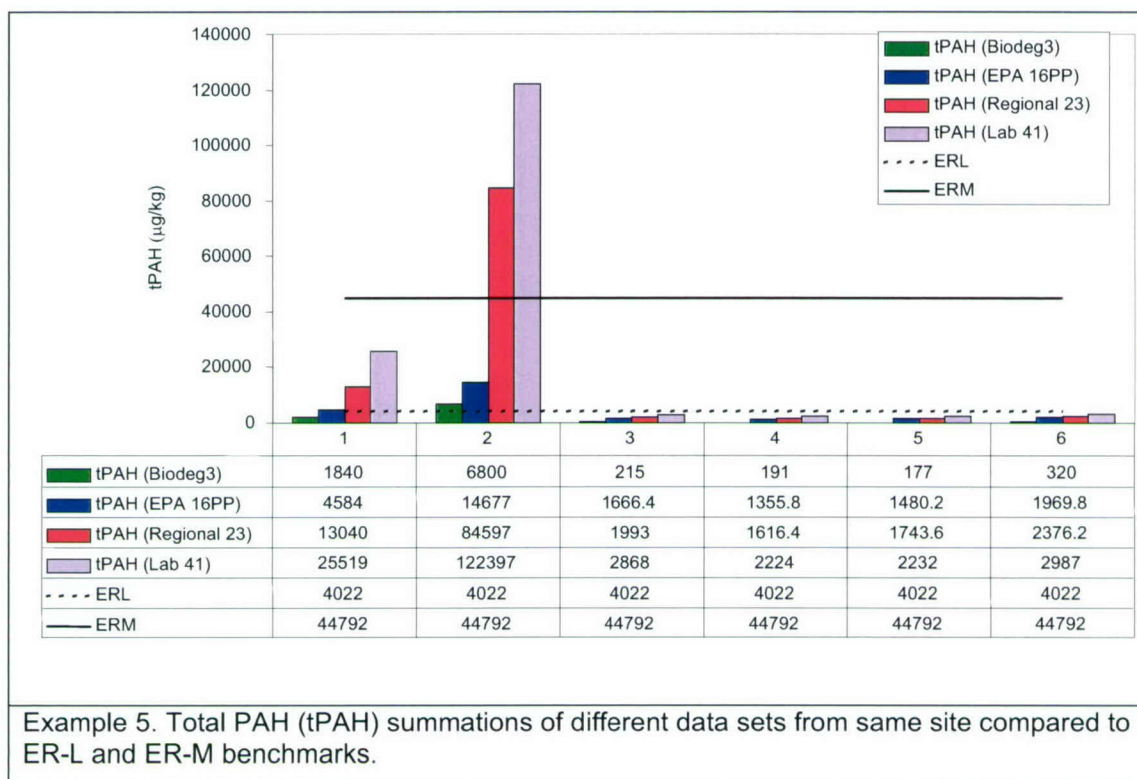
Many data reports compare the data to ER-L (lower 10th percentile of the effects data), ER-M (50th percentile of the effects data; values calculated in Long et al., 1995, and regional ambient values). These values are used as sediment quality criteria to aid in regulatory decisions. The data for the ER-L and ER-M calculations were taken from the biological effects database (BEDS), which compiles data from around the continental United States. When these values are used, care must be taken to determine the background concentrations for these contaminants. In particular, caution should be exercised when sediment Cr and Ni levels are compared to ER-L and ER-M levels. ER-L concentrations for Cr and Ni are 36% and 62% lower, respectively, than values for these two metals in average crustal rock (Wedepohl, 1995) and comparable with or lower than levels in mean marine sediment (Salomons and Förstner, 1984). In other words, any typical marine sediments will contain natural levels of Cr and Ni that exceed ER-L. In many ecological studies, metals are measured after a partial sediment digestion (appropriate for sorbed anthropogenic metals but not for bulk metals that might be part of the sediment matrix (Sinex, Cantillo, and Helz, 1980)). ER-Ls, which are a compilation of many studies, may be overly conservative for these

elements⁶. **Example 4** shows that average crustal abundances for Cu and Cr exceed ERL values and come close to sediment quality criteria for the states of Wisconsin and Washington. Clearly, regional source rocks may be well over or under these average abundances, so methods and criteria should be put in perspective of regional source conditions.

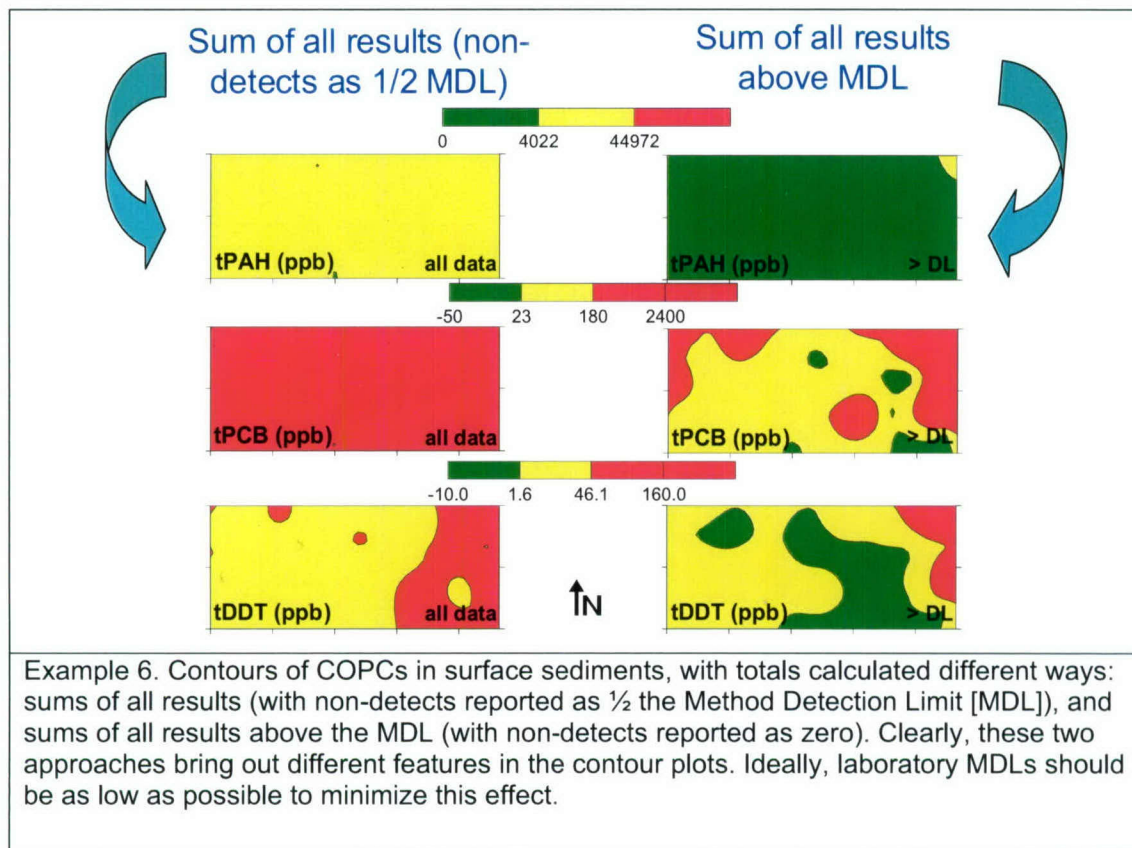


While metals in general are compared on an individual basis with candidate benchmarks, organic contaminants are broken into classes, which are then consolidated into summations. For instance, PAH can be subcategorized into “parent” compounds (compounds with two or more benzene rings but no alkyl or other rings attached—e.g., naphthalene, phenanthrene, benz(a)anthracene), or substituted compounds (polycyclic aromatic compounds with one or more alkyl or other substitutions on the rings—e.g., methyl naphthalene, diethyl phenanthrene, 1,3,7-trimethyl pyrene...). For PCBs, the story is even more complex because PCBs can be reported at Aroclor equivalents as individual congeners or as sums of various subsets of the possible congeners. Clearly, the possible permutations are endless. However, only some subset of these (those with available standards, established analytical methods, known toxicity, and/or ubiquity or abundance in the environment) are commonly regulated or monitored. Depending on the goals of a study or analytical resources available, different subsets of PAHs, PCBs, or pesticides are analyzed, but often these are reported as total PAHs (tPAH), etc. (**Example 5**). For site-to-site or site-to-benchmark comparisons, it is important that the same sets or subsets of compounds are included in summations, where possible.

⁶ J. Trefrey, personal communication.



To be protective, most environmental non-detect data are not reported as zero, but as $\frac{1}{2}$ the detection level. Marine sediments generally have cleanup criteria and contaminant levels significantly below those of regulated soils. If standard methods appropriate for soils are used, detection limits can be at or near many sediment benchmark criteria, and thus samples with non-detects reported as half such a relatively high detection limit can appear contaminated. This issue is magnified when sums of organic analytes such as total PAHs, total PCBs, or total DDTs are reported, because the sums of many non-detects reported as $\frac{1}{2}$ the detection limit can result in large numbers, making clean sites appear contaminated. These large numbers can make it particularly difficult to compare or contour organics data from different sources. As **Example 6** shows, if results from a laboratory with high detection limits are added and contoured as the sum of all numbers reported (with non-detects reported as $\frac{1}{2}$ detection limit), misleadingly high values can result, suggesting exceedances where they do not exist. Exclusion of data (including only values that are greater than the detection limit) will cause hotspot areas to stand out, but lose power to distinguish between very and moderately contaminated. These effects will also make it hard to meaningfully contour or compare results over time or from different studies unless it is ensured that methods and detection limits (as well as data reduction methods) are comparable. To minimize this effect (and the risk of useless data), laboratories with established records of trace analysis at levels appropriate for questions answered should be sought, even if this raises the cost of analyses.



2.6 SEPARATE SITE AND BACKGROUND CONTAMINANT LEVELS

Because of past industrial activities, ship activity, non-point source input, etc., sediments at numerous sites have some level of impact from anthropogenic compounds. Potentially responsible parties (PRPs) such as the Department of Defense (DoD) must assess and manage contaminated sediments to conduct dredging, transfer properties, or to clean up contaminated “hot spots.” While it is critical to address sites that pose a demonstrable and immediate ecological or human health risk, effective and equitable management decisions will depend on determining the contaminants’ source. In the case of the U.S. Navy, it is policy (Dave Olson, Chief of Naval Operations [CNO]) that the Navy will not do extensive work in contaminated sediments unless they know that they are responsible for the contamination. Due to the complexity of sediment management and the enormous potential costs nationally, many organizations have adopted such a policy. This point is important to a PRP from a liability/responsibility viewpoint, but more importantly, it is important because unless contaminant sources are identified, they cannot with confidence be effectively controlled. First, no sediment cleanup or management should begin until sources are controlled because unless all potential sources are identified and controlled, recontamination may occur. Second, if contaminants in a given unit of sediments do not reflect a unique local source, but reflect an accumulation of regionally contaminated “background” sediments, local remedial efforts will produce little or no ecological improvement. Bulk sediment contaminant concentrations and bioassay results, as currently examined and reported, are not effective at addressing these issues.

While absolute concentrations of COPCs in sediments are an important part of assessing site sediments, for many reasons, this alone does not provide a full picture of what is going on at the site. Organic and inorganic contaminants can exist in a region at background, ambient, or natural levels because they have natural sources, or because entire regions in urbanized, industrialized, and other areas are exposed to ubiquitous levels of anthropogenic input. In many cases, because such contaminants tend to associate with fine-grained sediments, a general regional tendency is to have a “mixing curve” of contaminated fines and relatively uncontaminated coarse-grained sediments. Often, ambient contaminant levels or background natural levels, or a combination of both, can be separated from site-specific levels by normalizing or plotting against sediment characteristics that tend to indicate natural metal-rich particles (e.g., Fe, Al) or fine-grained particles (e.g., Fe, Al, %fines, %OC). While ambient or background levels of COPCs can be bioavailable, and may cause ecological impact, they are almost impossible to manage for on a site-specific basis—cost and logistics make it improbable that an entire region will be remediated, and if specific sites are remediated to below ambient levels, those sediments will probably be subject to re-contamination by background sediments. Thus, it is important at a given site to examine contaminant distribution relative to regional, ambient, or background levels.

If sediment is of ecological or regulatory concern, this conclusion is most probably based on levels of COPCs that exceed a regulatory, literature, or site-specific toxicity threshold. However, it is not the bulk concentration of a contaminant that poses risk, but the fraction of that bulk concentration that is bioavailable. Thus, in assessing risk or a risk management approach for a specific COPC, it can be very important to determine the form in which the COPC resides in the sediment. If a COPC exceeds a chosen benchmark, it may be useful to determine what proportion of that COPC resides in a form that may be expected to be bioavailable, and what fraction resides in a less available form. If the bulk of the COPC is expected to be bioavailable, the small proportion that may not be bioavailable does not merit detailed investigation. On the other hand, if it appears that a significant portion of the COPC in sediment may reside in a non-bioavailable, natural, or unusual form, it is important to examine that portion and, perhaps, evaluate the risk (and management) of that portion of the COPC individually. Size fraction distribution can be one indicator of potential differences in availability or risk ([see SOP 3, Appendix A](#)). The most common association of contaminants is in the fine-grained sediment fraction and, thus, most field-related toxicity data have been generated with such sediments, and are thus reasonably applicable to these sediments. However, if contaminants are associated with a coarser fraction, they may be significantly less or more available than the fine-grain associated COPC. In cases where this is expected, this fraction merits a closer examination to determine the form a COPC takes in the sediment (for example, Apitz et al., 1999a and b). In **Case Study 2**, elevated levels of Cu were in the coarse fraction. Detailed examination of that fraction, using an SEM, revealed that elevated levels of the Cu in the coarse fraction were probably attributable to a naturally occurring mineral and not from an anthropogenic source.

CASE STUDY 2: SEPARATION OF SITE AND BACKGROUND LEVELS

Using Morphological Lines of Evidence to Separate Site and Background Levels

At this site, Cu, Pb, and Zn were measured in size-separated fractions of the sediment. By looking at the raw concentration of the metals in the different size fractions (Figure 2-1) and the mass normalized distribution (Figure 2-2), it can be observed that the metals are distributed throughout the grain sizes. This type of distribution suggests that there are potentially different sources, such as paint chips, blasting grit, etc., contributing to the overall concentration of metals in the sediment. A more detailed morphological examination of the sediment particles using Electron Dispersive X-ray Fluorescence (Figure 2-3) coupled with SEM (Figure 2-4) reveals evidence of Copper Sulfides (chalcopyrite). Today, around 80% of the world production of Cu derives from the treatment of chalcopyrite (CuFeS_2). In this case, the elevated levels of Cu found in the coarse fractions are most likely attributable to a naturally occurring mineral and not from an anthropogenic source. Such lines of evidence can be used to separate site and background levels of contaminants.

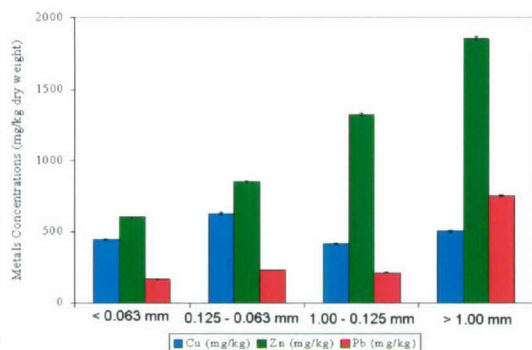


Figure 2-1. Metals concentrations.

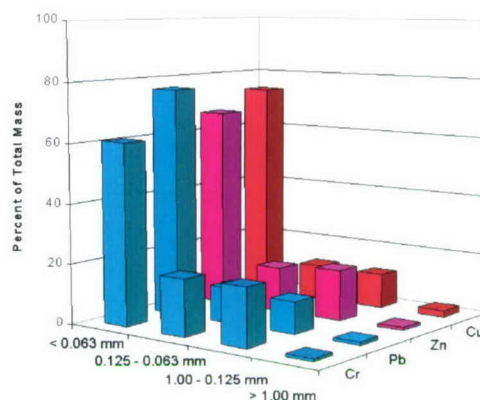


Figure 2-2. Mass distribution of metals.

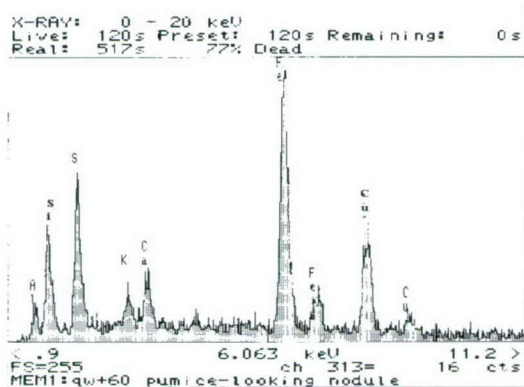


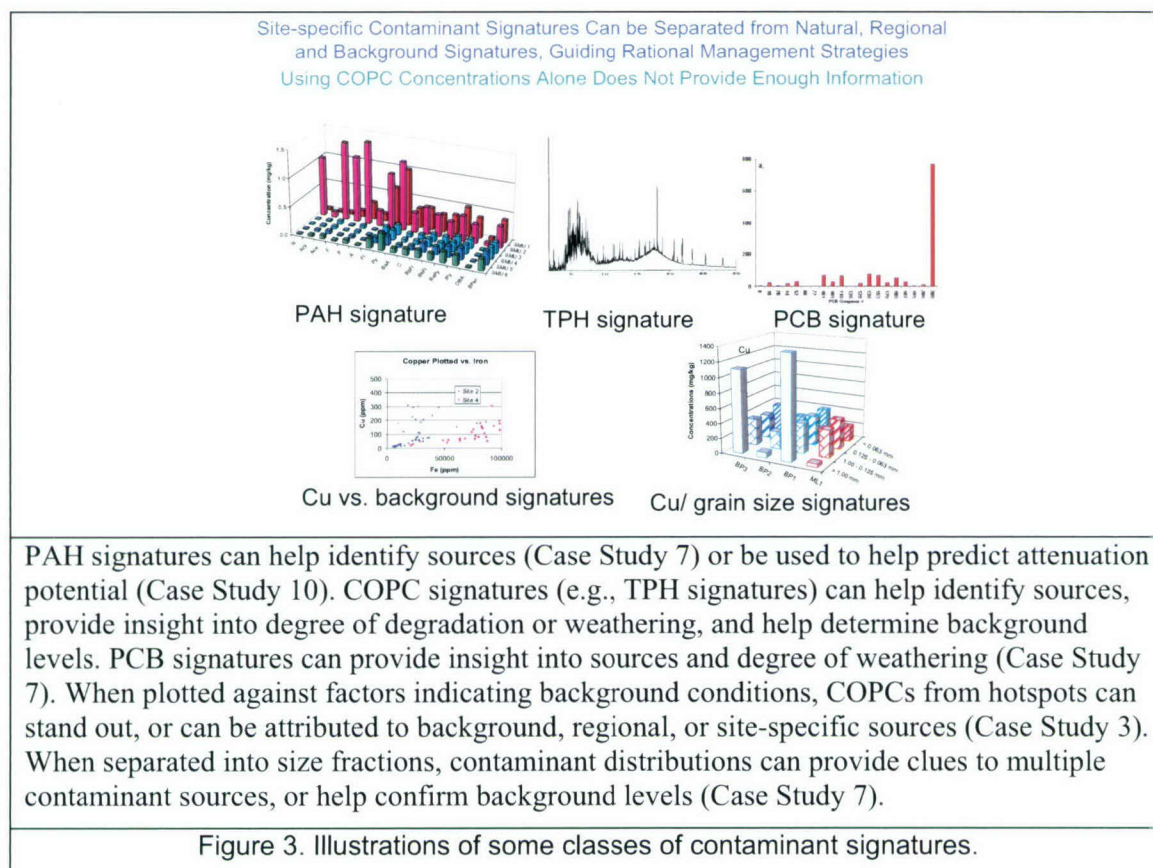
Figure 2-3. Electron dispersive X-ray.



Figure 2-4. SEM.

Normalizing contaminant levels to or plotting against sediment characteristics that tend to indicate natural metal-rich particles (e.g., Fe, Al) or fine-grained particles (e.g., Fe, Al, %fines, %OC) can provide insight into whether a given COPC has a site-specific source. However, that insight will not provide sufficient information to trace COPCs to a given source, which may be necessary to control sources, differentiate multiple sources, or to allocate responsibility. More detailed examination of contaminant signatures, such as the relative distribution of individual compounds in an organic mix, the isotopic signature of metals or organic compounds, or the presence or absence of various markers, can help elucidate these questions. For instance, while total PAH (tPAH) numbers are needed to compare to potential sediment quality criteria or benchmarks, the PAH fingerprint (the relative distribution of individual PAHs) can provide a significant amount of information on source, background, weathering patterns, potential toxicity, and the potential for natural attenuation (e.g., Page et al., 1995). Literature in environmental forensics is rich (e.g., see Morrison [2000] and his references). While this field has primarily focused on terrestrial sites, some work has been performed in marine sediments, and methodologies should be adapted and standardized for marine sediment systems (see section 3 for case studies).

Many kinds of contaminant signatures exist, and can be used for many applications. **Figure 3** illustrates a subset of these signatures (most are included in case studies in this report).



2.7 CONTAMINATED SEDIMENT MANAGEMENT: DATA "TRIAGE"

Generally, once some data are available, sediments of potential concern fall into the following three basic categories (if decision criteria were clearly laid out and negotiated):

1. COPCs are present, but at such low levels that there is no risk (or COPCs not present). If this is the case, detailed studies are not necessary, and a site can probably be set aside.

2. At least one COPC is clearly at high levels and poses an unacceptable risk. These sediments should not be subject to detailed risk analysis, but moved into the risk management arena. Further data collection should focus on more tightly delineating the two- or three-dimensional (depending on remedial options) COPC and toxicity distribution of the site, and information relevant to the FS.

3. "Grey area" sediments, where risk or extent are uncertain. At times, detailed studies of toxicity, availability, mobility, etc., are justified to determine degree and geographic extent of risk. These studies should focus on getting sites placed in one of the previous two categories. This goal is the main arena of the innovative and advanced sediment characterization tools, which may look at COPC distribution, bioavailability, mobility, or form in greater detail. Many sites tend to "brand" sites as toxic if benchmarks are exceeded or any toxicity "hits" are observed. Eventually moving Category 3 sites to Category 1 can create great resistance and suspicion, so decision criteria must be clear, negotiated, and transparent.

2.8 DATA FOR NOW AND FOR FUTURE

It is a regulatory requirement that presumptive remedies or assumed endpoints or cleanup levels do not drive ERAs. However, if data are not collected so the decision-makers, regulators, and managers can frame their decisions, unnecessary expense and delays occur. Before any but the most preliminary site assessment data are collected, all interested parties, including regulators, managers, etc., should negotiate their priorities, decision criteria, concerns, and limitations. Assessments should provide a stand-alone ERA and data to address concerns and guide decisions. No studies or measurements should be conducted within the RI/FS structure unless it is clear what role data will have in the decision and regulatory process.

However, sediment RI/FS studies are excellent opportunities on which to "bootleg" peripheral work funded by other projects to conduct R&D that will allow for better sediment management or the demonstration of innovative assessment or management tools. Such work can expand the scope or add site information, but even if results from such a peripheral study do not affect the decisions at the specific site, results and demonstrated methodologies may be useful for future sites. Given the dynamic and complex nature of contaminated sediment management, it is critical that technology, policy, and users are more closely linked so they can interface extensively, nationally, and within organizations. Most successful environmental technology requires at least a decade, from bench concept to acceptance and implementation. Most technology users, such as RPMs and regulators, are addressing problems that require some level of resolution within 1 to 3 years. The R&D community should, to a certain extent, provide an "informed push," rather than completely relying on users to anticipate long-term needs. Developers should be visionary, but willing to adapt projects, even under way, to regulatory and economic reality and change. Ultimately, need must guide the science and its end-goal must be a transfer to the next level of users (e.g., basic researchers to technology developers, technology developers to users) in a form that is useable and relevant to that community.

3. BIOGEOCHEMICAL CHARACTERIZATION WITHIN THE U.S. NAVY ECOLOGICAL RISK ASSESSMENT FRAMEWORK

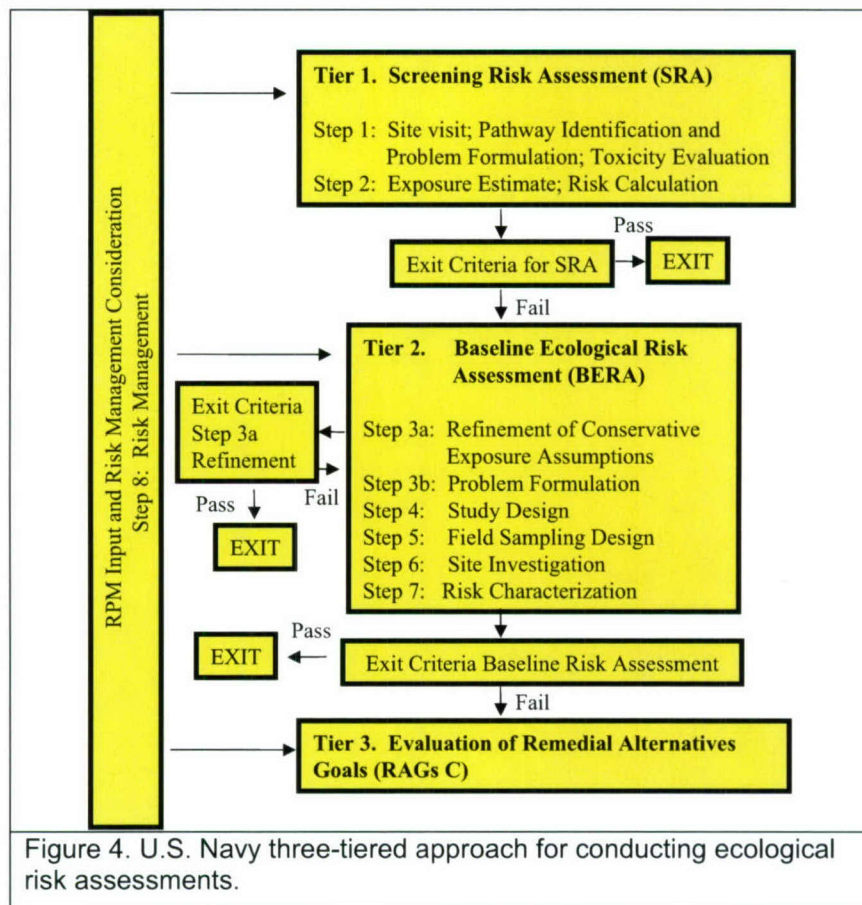
3.1 INTEGRATION INTO ECOLOGICAL RISK ASSESSMENT PROCESS

Ecological Risk Assessment (ERA) is the process that evaluates the probability that adverse ecological effects may occur or are occurring as a result of exposure to one or more stressors. Ecological Risk Assessments conducted by the U.S. Navy (and other organizations) before 1997 did not always adequately distinguish between risks posed by contaminants from U.S. Navy property and risks from other sites (non-Navy). The scope and problem formulation of ERAs were not well defined, resulting in costly and unstructured assessments with unnecessarily large scopes. Because of the complex nature of marine ecosystems and the limitations of currently available (pre-1997) techniques and methods, marine ERAs may not provide the information necessary to support decision-making. ERAs conducted for marine resources have not typically addressed natural attenuation. Despite the risk findings of marine ERAs, few realistic, active remedial options were available, and they were hard to select.

Specific policies regarding the implementation of ERAs at U.S. Navy sites are as follows (see <http://web.ead.anl.gov/ecorisk/policy/pdf/policy.pdf> for complete document):

- ☐ ERAs should focus on ecological risks from past and current exposure pathways from U.S. Navy sites, and consider contaminant loadings from all significant sources and pathways, thus permitting mass balance evaluations for identifying U.S. Navy and non-Navy contaminant contributions.
- ☐ Source control and best management practices should be used to prevent additional contaminant releases.
- ☐ Sampling programs should focus primarily on the identification of potential contaminant sources and on delineating areas of contaminated media.
- ☐ Sampling programs should use advanced chemical and biological screening technologies, data quality objectives, and statistical procedures to minimize overall sampling requirements.
- ☐ Large-scale water column sampling programs should be warranted only if there is a major issue regarding contaminant flux or contaminant source determination.
- ☐ If the regulators require long-term monitoring, well-defined exit criteria must be identified and included in the agreement.
- ☐ If non-Navy contaminant sources are identified, the U.S. Navy policy is to avoid implementing monitoring programs with exit criteria based on contaminant concentrations declining to some specified levels.
- ☐ If the screening results identify the need for an ERA, an evaluation of natural attenuation should be included in the ERA.

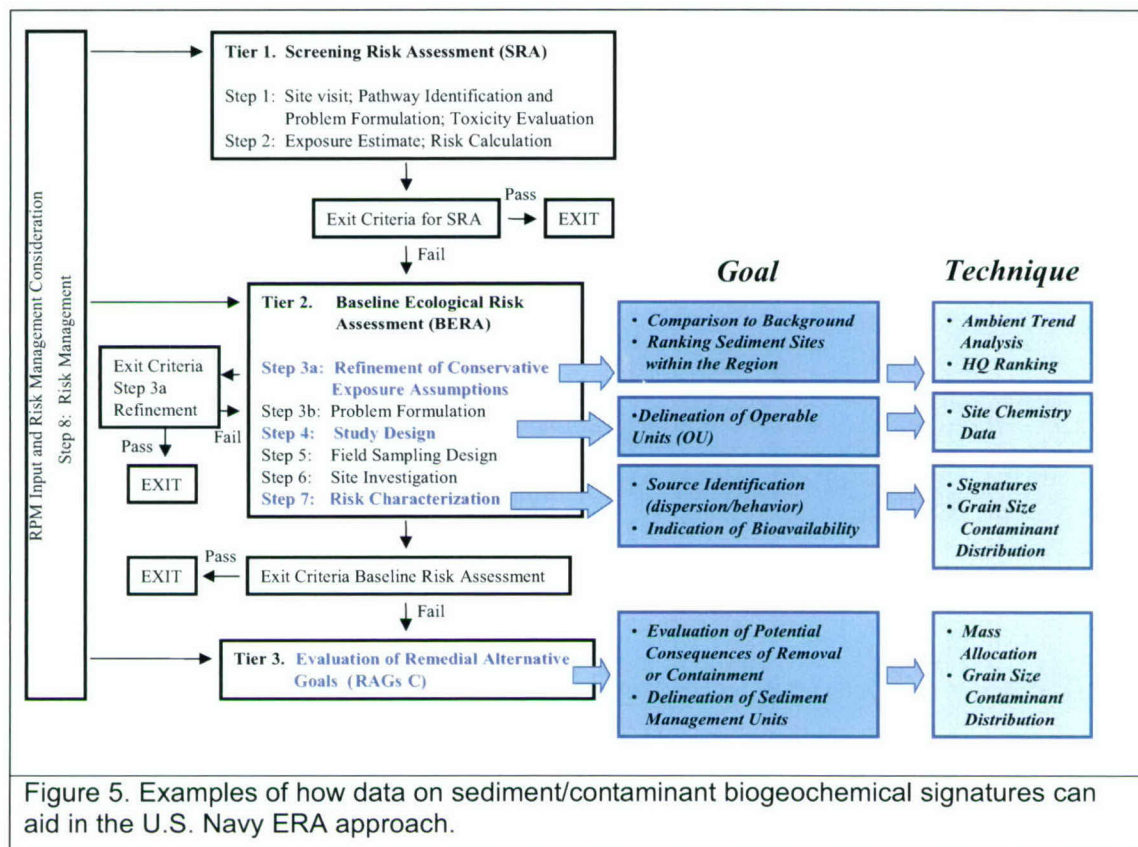
In response to these needs, the [Chief of Naval Operations \(CNO\) Policy for Conducting ERAs](#) (as of 5 April 1999) identified a three-tiered approach that incorporates different levels of assessment complexity. **Figure 4** illustrates this approach.



The tiered approach begins with conservative assumptions and existing data to evaluate potential risk. The ERA proceeds to the next tier (greater level of assessment complexity) only if earlier tier results warrant it. The tiered approach requires clearly defined problem statements, risk hypotheses, and data needs, thus avoiding “shotgun” data collection and/or collection of data that do not address the proposed problem.

While the U.S. Navy and other organizations are developing sediment policy and guidance, significant technical gaps limit sediment risk assessors’ and managers’ ability to address sediments cost-effectively. The understanding of site-specific contaminant/sediment geochemical interactions and appropriate use of these data in decision-making and negotiation are among the many tools that help address these issues and policies more effectively. This report provides site owners with examples of how to use site-specific data to compare site, background, and regional sediment signatures to address risk, determine responsibility for inputs, rank sites, and prioritize management; to help bridge the gap between remedial investigations and feasibility studies in a meaningful way; and to provide site owners with the tools to rapidly determine what sediment management approaches are feasible for contaminated sediments at their sites—and to use site data to evaluate, communicate, and negotiate management choices. This section highlights some of the major uses for data on contaminant/sediment geochemical interactions in the assessment and management of contaminated sediments within the U.S. Navy’s tiered approach.

Figure 5 illustrates some of the points within the U.S. Navy's tiered approach at which data on contaminant/sediment geochemical signatures can aid in evaluation.



3.2 STEP 3A: REFINEMENT OF EXPOSURE ASSUMPTIONS

The purposes of Step 3a are to re-evaluate the COPCs retained from Tier 1 for further evaluation in a Tier 2 Baseline Risk Assessment (BERA) and to identify and eliminate from further consideration those COPCs retained because of very conservative exposure scenarios. Using less conservative (but more realistic) assumptions, the risk assessor recalculates the Tier 1 risk estimates and uses these new estimates to refine the list of COPCs identified by the Tier 1 Screening Risk Assessment (SRA) to remove some or all COPCs from further consideration.

Step 3a involves the re-evaluation of the Tier 1 SRA COPCs with less conservative but more realistic assumptions regarding exposure. Successful conduct of this step involves technical interactions with the regulators, and will require regulator concurrence before any COPC may be dropped from further evaluation. In addition, the re-evaluation should also evaluate the Tier 1 risks with regard to background risks (do site contaminant concentrations exceed background levels?), the magnitude and extent of the contamination and risk (are high concentrations and risks widespread across the site or limited to discrete locations?), and bioavailability of the COPC (Could the COPC be in a chemical form that is less hazardous?

Could the COPC be bound to sediments so that it cannot be taken up by biota?) (<http://web.ead.anl.gov/ecorisk/process/pdf/index.cfm>).

3.2.1 Background Levels

Biogeochemical sediment characterization can be used for further evaluation of COPC exceedance of background levels and extent of contamination. However, the evaluation of bioavailability is difficult because so many different factors may affect bioavailability factors and bioavailability varies from contaminant to contaminant. Evaluation of this parameter is relatively difficult and problematic. Additional information on evaluation of bioavailability within the risk assessment framework is available at <http://newweb.ead.anl.gov/ecorisk//>.

As stated in the Navy Interim Final Policy on the Use of Background Chemical Levels⁷, “Background evaluations should be conducted during the site investigations in order to differentiate between the Navy’s cleanup responsibilities and background sources. The COPC selection process includes elimination of chemicals on the basis of background evaluation. As part of this evaluation process, it is important to identify background sources, differentiate between naturally occurring and anthropogenic sources and finally compare site levels to background levels. If site levels do not exceed background, then the COPC can be eliminated from further evaluation.” This document is available at the following Web site: (<http://web.ead.anl.gov/ecorisk/policy/pdf/bkgpolicy.pdf>).

While absolute concentrations of contaminants in sediments are an important part of assessing site sediments, for many reasons, these absolute concentrations do not provide a full picture of what is occurring at the site. Organic and inorganic contaminants can exist in a region at background, ambient, or natural levels because they have natural sources or because entire regions in urbanized, industrialized, and other areas are exposed to ubiquitous levels of anthropogenic input. In many cases, because such contaminants tend to associate with fine-grained sediments, a general regional tendency is to have a mixing curve of contaminated fines, and relatively uncontaminated coarse-grained sediments (Förstner, 1987; Bergamaschi et al., 1997; Galloway and Snitz, 1992; U.S. EPA, 1992). Ambient contaminant levels or background natural levels, or a combination of both, can often be separated from site-specific levels by normalizing to or plotting against sediment characteristics that tend to indicate natural metal-rich particles (e.g., Fe, Al) or fine-grained particles (e.g., Fe, Al, %fines, %OC). While ambient or background levels of contaminants can be bioavailable, and may cause ecological impact, they are almost impossible to manage on a site-specific basis—cost and logistics make it improbable that an entire region will be remediated, and if specific sites are remediated to below ambient levels, those sediments will probably be subject to recontamination by background sediments. Thus, it is important at a given site to examine contaminant distribution relative to regional, ambient, or background levels, and to select reference sites with care (Apitz et al., 2005a and b).

The scientific basis and methodologies for background normalization are well established (Förstner, 1987; Bergamaschi et al., 1997; Galloway and Snitz, 1992; U.S. EPA, 1992). Guidance on methodologies, with an emphasis on soils, is available at the following Web site: http://enviro.nfesc.navy.mil/erb/erb_a/restoration/methodologies/bg_soil_guide.pdf.

However, as it is in guidance, trend analysis alone should not be used to eliminate COPCs unless some mechanistic understanding of the correlation exists. In short, does the CSM in

⁷ Chief of Naval Operations (CNO). 1999. “Navy Interim Final Policy on the Use of Background Chemical Levels,” Ser N453E/0U595690, Washington, DC.

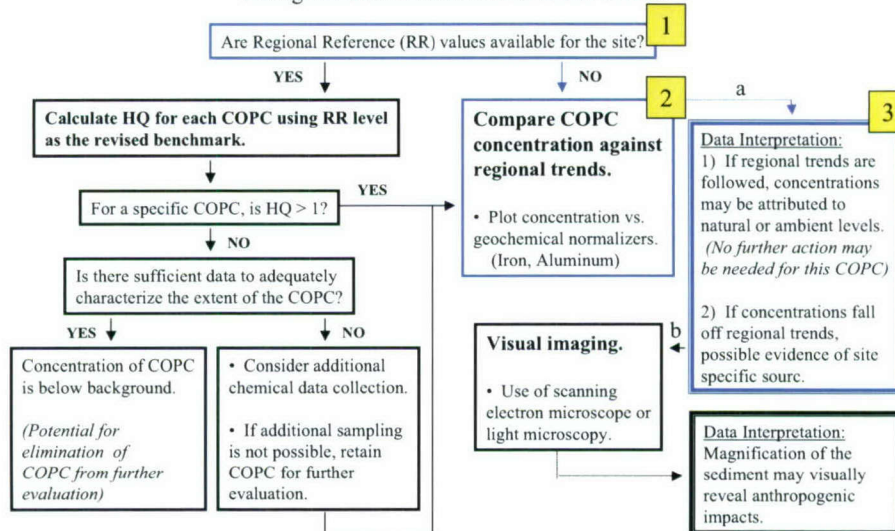
some way explain why, for example, Cu in the sediments should correlate with Fe? Does such a correlation exist in the source rocks or their weathering products? In all cases, note that contaminants could co-associate or be co-deposited with the elements to which they are normalized. Further lines of evidence on COPC source, form, and/or bioavailability should be considered to support management decisions.

In **Case Study 3**, Ambient Trend Analysis, a standard geochemical data analysis technique answers the following question: Do site contaminant concentrations exceed background levels? As [Chart 1 \(Appendix B\) shows](#), COPC concentrations can be plotted against geochemical normalizers such as Fe to determine if the concentrations may be attributed to natural or ambient level (i.e., background). Once it has been determined that metals in one region correlate with Fe, while those in another do not, other lines of evidence are applied to develop a mechanistic understanding of the metal sources (**Case Study 3 addendum**).

The same technique can be applied to organics data (**Case Study 4**). As discussed above, the tendency for organic contaminants to associate with natural organic matter (NOM) and high surface area sediments means that if a regional, background level of COPCs exists, they will have a linear relationship with those sediment components that correlate with organic-rich fines (%OC, %fines, Fe, etc.). In **Case Study 4**, organic contaminants are normalized to total organic carbon (TOC) ([Chart 2, Appendix B](#)). The implication is not that some organic COPCs have natural sources, but that the organic COPCs are normalized to try to separate ubiquitous, regional levels of contamination from site-specific sources. While it may be possible to remove or remediate site-specific contaminant levels, a regional distribution of COPCs is probably too widespread, diffuse, or costly to manage. Such a contaminant distribution should be addressed with large-scale regional source control and, over time, natural attenuation. However, when samples from a unit of sediment clearly lie above the regional trend, it suggests possible site-specific sources of contaminants. Other lines of evidence can then be applied to establish this site-specific source. One important tool that examines the possibility of different sources or weathering patterns is contaminant signatures.

CASE STUDY 3: METALS BACKGROUND

Chart 1: Step 3a: Refinement of Conservative Exposure Assumptions;
Background Considerations for Metal COPCs



In this case study, Cu and Pb were identified at metal COPCs, but regional reference levels have not been assigned (box 1 in flowchart above). To compare COPCs to background levels, Cu (Figure 6-1) and Pb (Figure 6-2) were plotted against Fe (2). Cu and Pb in most samples from Region 2 and some from Region 1 correlate with Fe, but many samples from Region 1 show a dramatic deviation from the ambient trend. In Region 1, Pb and Cu should be retained for further evaluation. In Region 2, because Cu and Pb follow ambient trends, a case exists for removing them as COPCs in this region. See the Case Study 3 addendum for a further evaluation of lines of evidence that can supplement these conclusions.

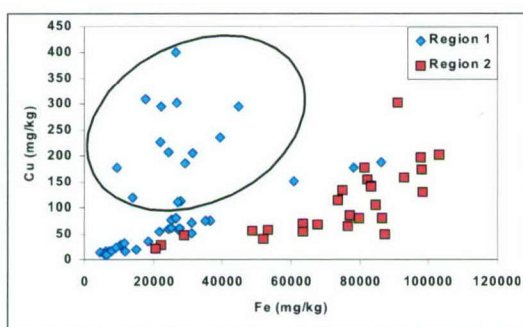


Figure 6-1. Copper normalized to iron.

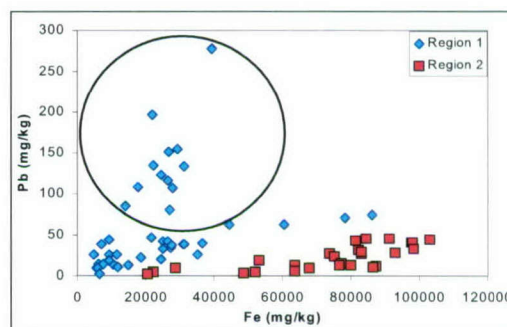
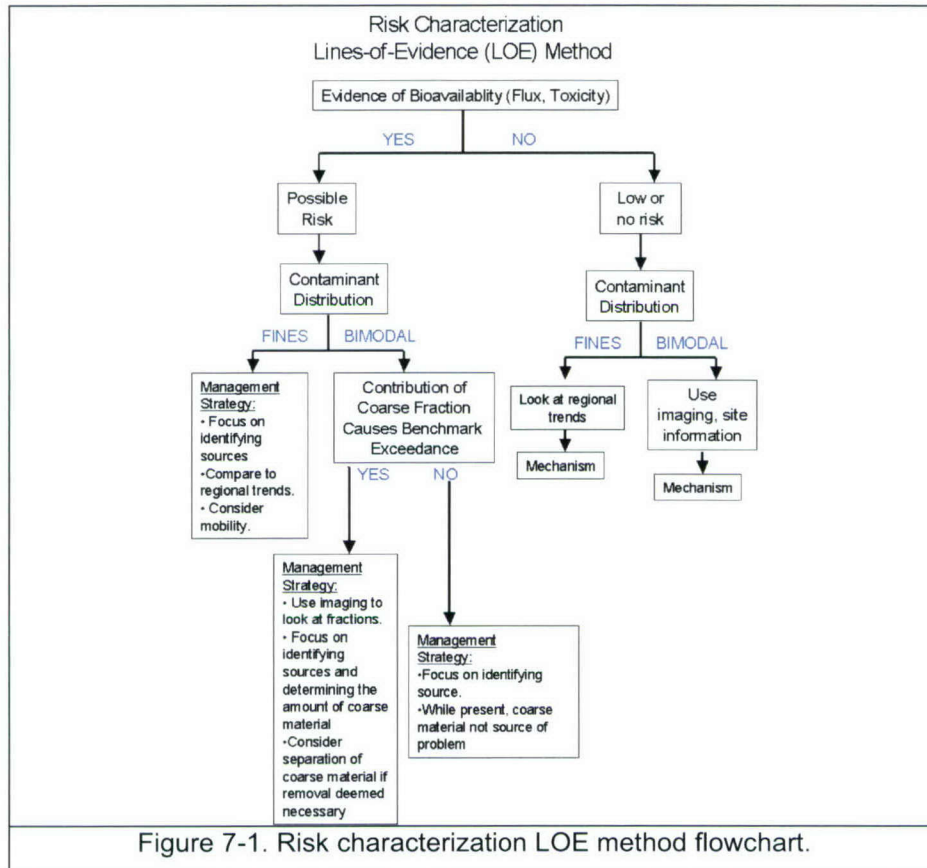


Figure 6-2. Lead normalized to iron.

Note: Correlations (or lack thereof) can be coincidental, so a reasonable mechanistic explanation or other lines of evidence are needed to make conclusions believable. See the Case Study 3 addendum.

CASE STUDY 3 ADDENDUM: METALS BACKGROUND ADDENDUM

Lines of Evidence for Regional Trends



The risk characterization LOE method flowchart (Figure 7-1) illustrates how supporting data on metal/sediment interactions and behaviour can be used. Elevated levels of Cu at Region 2 (correlating with Fe) can be attributed to volcanic sediment source (see Figure 7-2). Other lines of evidence must be examined to eliminate Cu at Region 2 and examine excess at Region 1. Cu in Region 1 fluxes across the sediment/seawater interface at much higher rates than in Region 2, even though bulk sediment Cu concentrations were equivalent, suggesting Cu was more “available” in Region 1, immobile in Region 2. This finding bolsters the case for eliminating Cu as a COPC in Region 2.

The high Cu in Region 1 (not correlating with Fe) must be examined to determine possible form and source (Figure 7-3). Contaminant mobility was indicated by positive flux. Toxicity was also higher in this region. Contaminant distribution as a function of grain size was examined to evaluate the form and source of Cu. A significant proportion of the Region 1 Cu (~50%) is in the coarse-grained material. Because this is a ship-berthing site, coarse-grained, mobile Cu can be attributed to anti-fouling paint chips. This Cu-bearing sediment would be managed differently than the Cu-rich fines, which are in all regional sediments, and are probably naturally occurring.

CASE STUDY 3 ADDENDUM (continued)

Lines of Evidence for Regional Trends

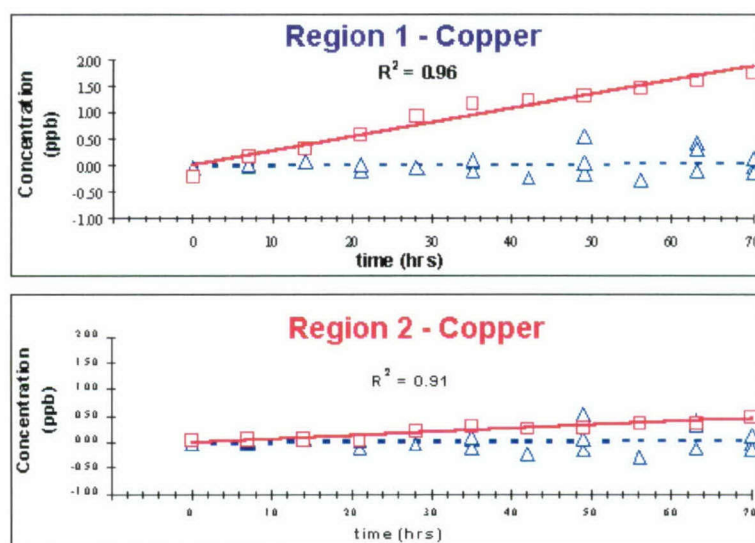


Figure 7-2. Flux of Cu across the sediment/seawater interface for Region 1 and Region 2 sediments with equivalent bulk sediment Cu concentrations, but different Cu/Fe ratios.

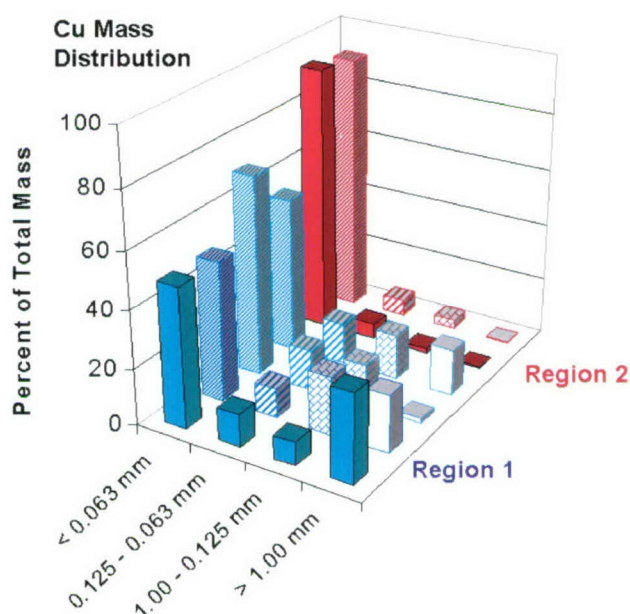
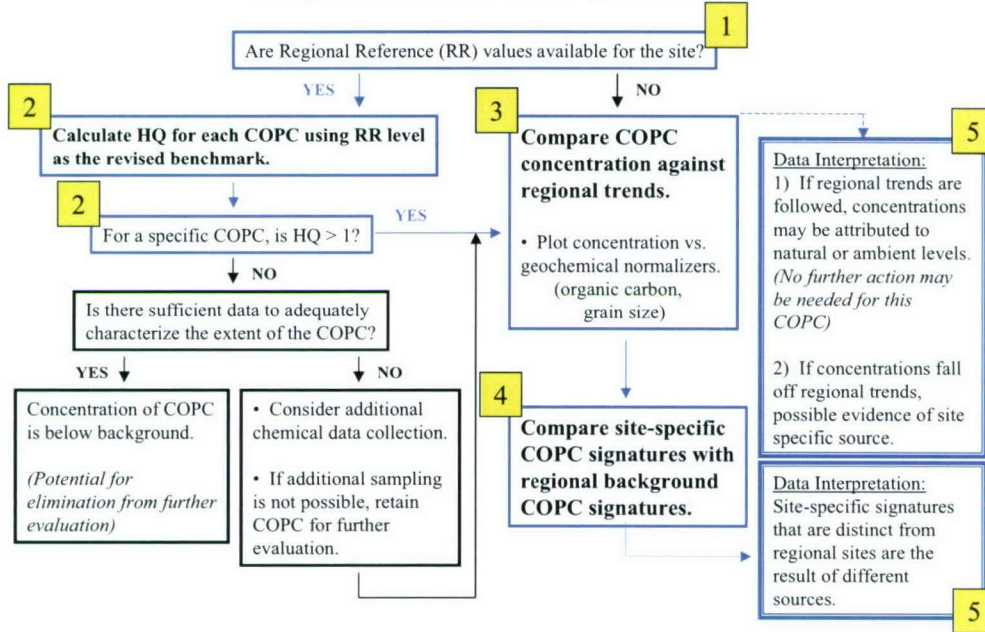


Figure 7-3. Mass distribution of Cu in coarse- and fine-grain sediment fractions from Region 1 and Region 2 sediment samples.

CASE STUDY 4: ORGANICS BACKGROUND

**Chart 2: Step 3a: Refinement of Conservative Exposure Assumptions;
Background Considerations for Organics COPCs**



At this site, PCBs are the principal organic COPC. Extensive studies in this area have resulted in the development of Regional Reference Levels (1). Using the Regional Reference Level for total PCBs as the selected benchmark, a Hazard Quotient ($HQ = \text{COPC concentration} / \text{benchmark concentration}$) can be calculated (2) (Figure 8-1). Areas for which the $HQ > 1$ are flagged for further analysis. The COPC can also be compared against a geochemical normalizer such as Total Organic Carbon (TOC) to determine if the COPC exceeds background levels (Figure 8-2) (3).

Sample ID	Total PCB (ppb)	RR85 tPCB (ppb)	HQtPCB
1	186.67	7.2	25.9
2	140.68	7.2	19.5
3	48.31	7.2	6.7
4	43.49	7.2	6.0
5	31.82	7.2	4.4
6	1267.6	7.2	176.1
7	350.25	7.2	48.6
8	202.92	7.2	28.2
9	41.38	7.2	5.7
10	26.73	7.2	3.7
11	59.09	7.2	8.2

Figure 8-1. PCB hazard quotients.

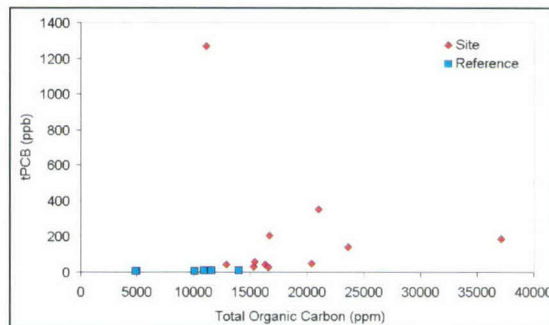


Figure 8-2. Regional trend comparison.

3.2.2 Refinement of Conservative Exposure Assumptions

Detection frequency refers to the percentage of total samples of a particular media in which the COPC was detected. In the Tier 1 SRA, detection frequency is not considered, and only the maximum reported concentration is used to estimate risk. However, if a particular COPC was detected only in a very small percentage of the samples collected, the risk identified in the SRA may be greatly overestimated. Chemicals that are infrequently collected may be artifacts related to sampling or analytical problems, or may be reflective of a contaminant hot spot (i.e., discrete area of very high contaminant concentration) rather than widespread contamination. In such an instance, a decision to delete the COPC from further evaluation or to initiate a very selective cleanup may be appropriate. Elimination of COPCs on the basis of detection frequency is not uncommon in human health risk assessments, and Section 5.9.3 of the EPA Risk Assessment Guidance for Superfund (RAGS): Part A—Human Health Evaluation Manual (U.S. EPA, 2004) provides additional discussion regarding criteria for evaluating detection frequency during COPC identification. RAGS Volume 1 can be viewed or downloaded at <http://www.epa.gov/superfund/programs/risk/ragsa/index.htm>.

Site data (chemical, physical, biological) can be used during this step of the ERA to delineate potential OUs to evaluate the magnitude and extent of contamination and risk at the site and to determine if the high concentrations and risks are widespread across the site or limited to discrete locations ([Chart 3, Appendix B](#)). In the following example (**Case Study 5**), site chemistry data for five metal COPCs were used to characterize the extent of contamination for each COPC. Hazard quotients and detection frequency analysis were used to spatially characterize the extent of contamination for each COPC. In doing so, a determination as to hotspot contamination versus widespread contamination for each COPC could be observed.

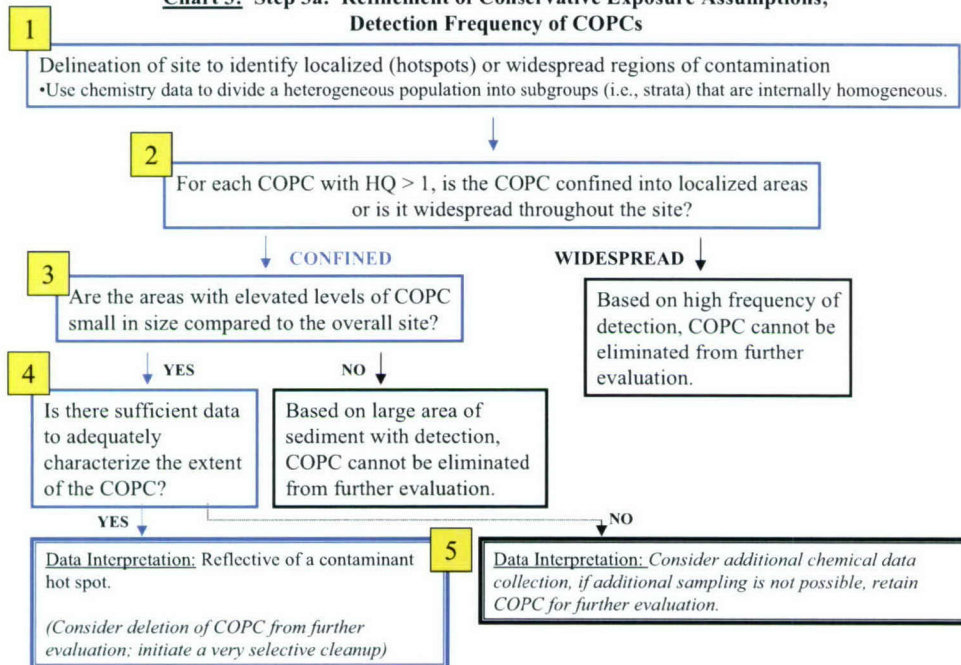
3.3 STEP 4: STUDY DESIGN AND DQO PROCESS

Step 4 of the U.S. Navy ERA process represents the identification and design of the scientifically defensible site-specific investigations necessary to address the risk hypotheses and risk questions previously developed. Activities associated with Step 4 include the following:

- ❑ Identification of specific data needs
- ❑ Selection of assessment endpoint-specific measurement endpoints
- ❑ Determination of the type and amount of the needed data
- ❑ Identification of the acceptable levels of uncertainty related to the data needs
- ❑ Identification of specific methods for collecting and analyzing the data
- ❑ Selection of the appropriate risk characterization approach
- ❑ Selection of specific study methods (i.e., toxicity tests, field surveys, tissue analyses)

CASE STUDY 5: DETECTION FREQUENCY

Chart 3: Step 3a: Refinement of Conservative Exposure Assumptions; Detection Frequency of COPCs



At this site, many samples were taken ($n = 60$). Site chemistry data for the metal COPCs (Cu, Cr, Cd, Zn, Pb) were used to divide the site into areas of similar levels of contamination (1). Hazard quotients for each COPC were calculated using ERM values (2). The detection frequency for each of these COPCs was calculated. All metal COPCs, with the exception of Cu, had HQs greater than 1.0 for a percentage of the total samples (Figure 9-1) (3). The data were also plotted spatially to characterize the extent of contamination for each COPC (Figure 9-2) (4). The COPCs with HQ>1 (Cr, Cd, Pb and Zn) are predominantly confined to two small regions (hotspots) (5). Copper was not detected in any samples at levels that exceeded an HQ = 1.0. It is possible that this information could be used to support the removal of Cu from the COPC list.

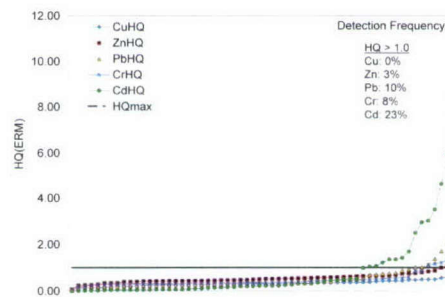
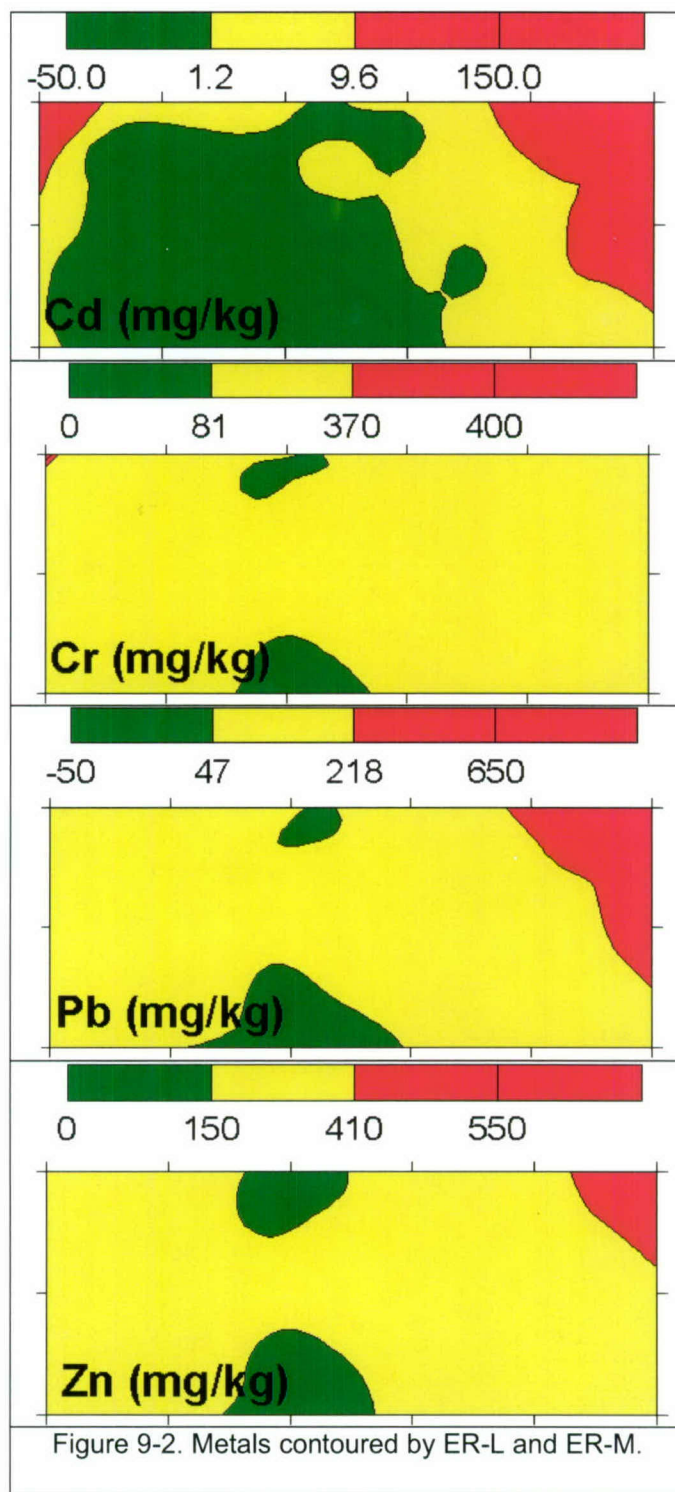


Figure 9-1. Detection frequency for metal COPCs.

CASE STUDY 5 (continued)



The completion of these activities generates data quality objectives (DQOs) that clarify the data requirements for future field sampling plans. This DQO process avoids a study design that produces data that do not address the site decision/risk questions.

Two key steps in the DQO process are the identification of the number of samples collected and the sample collection method. The investigation of surface and depth data is a fundamental approach for defining these steps.

3.3.1 Surface Versus Depth or Core Data, and Conversion Between the Two

In an ideal world, sediments under study would always be sampled and analyzed at high density, in three dimensions (over an area and with depth). However, due to high costs and funding limitations, sampling plans are often limited. There is extensive literature on approaches to environmental sampling (see, for example, Gilbert, 1987). However, sampling plans should be tailored for the questions being asked. If possible, sampling and analytical plans should anticipate multiple uses of data, and accommodate them to avoid unnecessary, iterative sampling. At times, it is much more cost-effective to do a more in-depth sampling up front to avoid more sampling later. Even if initially more data are collected at higher cost due to higher density, resolution, and quality of analysis, within reason, they will generally pay for themselves by minimizing iterative sampling, reducing the probability of “surprises” such as hotspots, buried contaminant peaks, and inaccurate volume estimates, and providing data for multiple uses throughout the RI/FS process. Except during the most preliminary screening assessment, future data needs must be considered in designing sampling and analytical plans. Thus, ALL players along the decision process, from risk assessors to risk managers, should be consulted in design.

For most initial risk assessments, the focus is on surface sediments that are most directly in contact with biota. A more detailed risk assessment, however, as well as the evaluation of remedial options, often requires information about contaminant distribution with depth. Such information requires core samples.

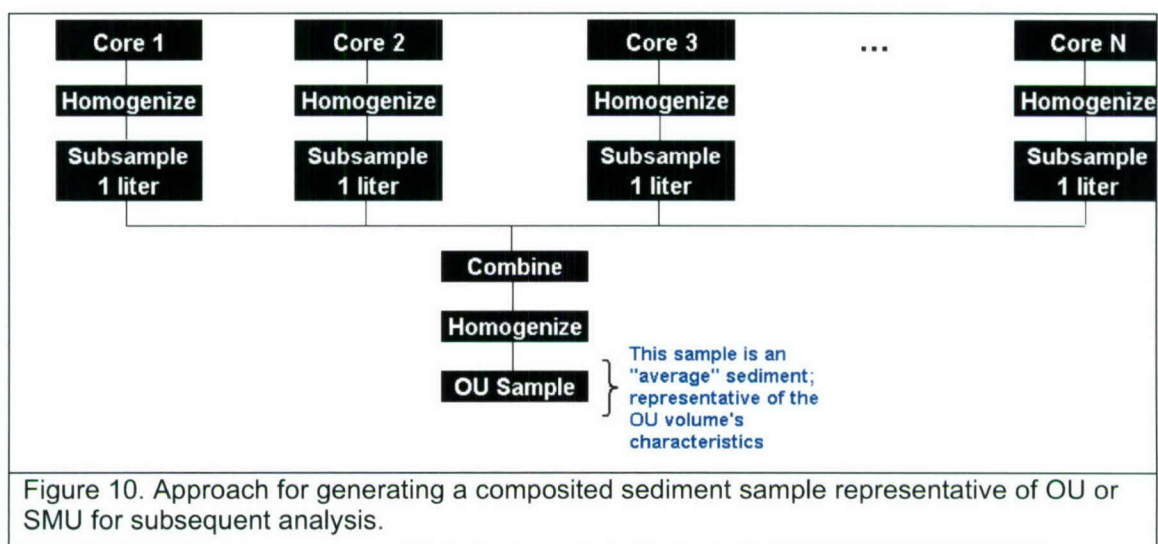
For screening risk assessments, individual sediment data points are evaluated. Later, in the refinement of risk assumptions, these individual data points will be examined in terms of detection frequency to determine how representative they are of regions or units of sediments (see below). However, it is important to remember that units of sediment, not individual samples, will ultimately be managed, so a broader risk assessment, or the evaluation of management strategies, must consider sediment as operable units with regional or average characteristics, rather than focusing on single samples. It is thus important to sample and analyze sediments so they can provide the most adaptable information affordable, and, as appropriate, convert from one sort of data to another.

Thus, sediments can be sampled in the following ways:

- ☐ Surface grabs, which are relatively easy and cheap to sample, but provide no depth information
- ☐ Composited cores, which provide information about a unit of sediment, but provide no information about peaks or gradients
- ☐ Sliced cores, which provide the most resolution (they can either be continuously sampled or sampled at intervals), but are the most expensive in sampling and analytical terms

If the consequences of sediment removal, erosion, or mixing are being considered, or if one is asking long-term stability questions in a risk assessment or remedy selection, it is critical that depth information of the highest resolution affordable be applied. Data can then be used selectively to address different questions.

If the characteristics of a unit of sediment are required to evaluate remedial options, and resources are limited, then single cores or cores from a defined OU (otherwise called a sediment management unit [SMU]) can be composited before analysis. Figure 10 shows one approach to compositing cores from an OU. While this approach is cheaper than the analysis of multiple core samples, much potentially useful information about gradients is lost. On the other hand, because potential removal, transport, or treatment of sediments is applied to volumes of sediments, this method provides analyses of a unit to be managed.



If multiple cores or sectioned cores are used for analysis, the data can then be averaged and/or weighted to generate data on sediment units. This approach provides critical data on three-dimensional distributions of contaminants in sediments, but still allows for the generation of volume estimates.

A procedure can be followed that provides an example of how depth data can be converted into concentration values for a unit of sediment ([see SOP 1, Appendix A](#)). Steps 1 through 3 of this SOP delineate the contaminant depth profile within a site. This delineation of depth data can be used in future mass balance calculations.

3.4 STEP 7: RISK CHARACTERIZATION

At this point in the BERA, the data and results obtained during the Site Investigation and Analysis phase (Step 6 and prior data) are integrated into one or more conclusions about the risks to the assessment endpoints and are used to answer the risk questions developed during problem formulation. This risk characterization provides the basis for the RPM to make a risk management decision about the site.

Three methods are commonly used to estimate ecological risk:

- ❑ Hazard Quotient (HQ)
- ❑ Lines of Evidence (LOE)
- ❑ Weight of Evidence (WOE)

The Tier 2 BERA will typically evaluate many measurement endpoints for each assessment endpoint identified in problem formulation. However, the results of these evaluations may not readily support risk estimation using the HQ approach. The risk assessment team must integrate the different types of data and results for the measurement endpoints into a risk estimate for each assessment endpoint. The LOE method represents an approach for integrating these dissimilar data and results into a risk estimate. The LOE approach evaluates all qualitative and quantitative information for each measurement endpoint (i.e., toxicity tests, uptake modeling, field studies, tissue concentration measurements, etc.) and applies professional judgment to provide a single qualitative risk estimate for the assessment endpoint.

Although not a standard data set, size fraction distribution data can lend further insight into the potential differences in availability or risk of the COPC. Understanding the grain size association of contaminants can be important for many reasons. A bimodal distribution may indicate that contaminants come from more than one source. If contaminant sources are not controlled before other management strategies are put in place, re-contamination may occur. In addition, metals associated with coarse sediment fractions often (but not always) have different solubility and bioavailability than those sorbed onto surfaces. Thus, any risk assessment done for these contaminants should not be done based on bulk concentrations, but rather should consider the different “types” of a given contaminant in the system. To do this procedure correctly, chemical results in the various sediment fractions must be combined with other parameters, such as the examination of contaminant form, sediment toxicity, bioaccumulation potential, and possible contaminant fluxes in the different OUs. An examination of the potential risk of different “forms” of the COPCs can provide qualitative and quantitative information for different measurement endpoints evaluated during the LOE approach. For instance, in **Case Study 2 (Section 2.6)**, a Benthic Flux Sampling Device (BFSD) found exceptionally high Cu to be very immobile. At this site, coarse-grained Cu-rich particles contained Cu that was *less* mobile than that sorbed to fine-grained particles, based on toxicity, bioaccumulation, and BFSD studies. SEM imaging and elemental analyses of particles determined that the high Cu was in the form of highly insoluble Cu sulfides, resulting from ore spills during ship loading. Such Cu should be subject to different risk benchmarks than more mobile Cu, and may not require treatment or removal. On the other hand, the high Cu in Region 1 of Case Study 3 was shown (using BFSD) to have higher mobility than the fines-associated Cu in Region 2 (**see Case Study 3 addendum, Section 3.2.1**). Research into potential input sources suggested that the coarse-grain-associated Cu at the site could be attributed to chips of anti-fouling paint. This form of Cu is highly mobile.

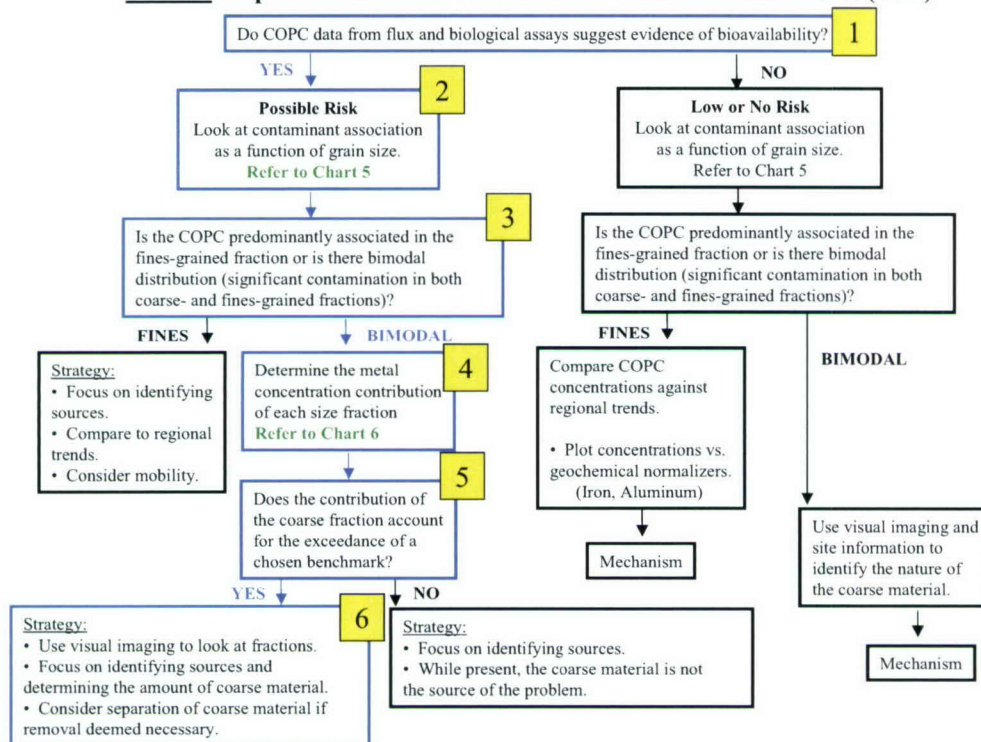
In the case of metals, the large concentrations associated with some of the coarse-grained sediment fractions might indicate the need for a more detailed examination of that fraction. To justify more detailed examination of the coarse-grained fraction, it is necessary to use the sediment concentration and fractions data to determine whether this fraction alone could be expected to account for exceedance of a chosen benchmark ([Charts 4-6, Appendix B](#)). This fraction is calculated from the relative distribution of the metal in each size fraction and the certified concentration in the bulk sediment ([see SOP 3, Appendix A](#)). **Case Study 6** shows the concentration of Pb that can be attributed to each size fraction in the OUs. While regional

reference levels, ER-L and ER-M, are also plotted, size fraction distributions are not available for these benchmarks because they are a composite of many sediments. The fines-associated Pb alone exceeds regional reference levels in OUs 1 through 5, but not other benchmark values. Pb associated with the coarse-grained fraction in these sediments is substantial as well; the Pb associated with the coarse-grain fraction alone in OUs 1 and 2 exceeds all SQGs. Physical separation of coarse-grained sediments from the fines in OUs 1 and 2 would result in reduction of Pb in the remaining sediments to ER-M levels, and to below ER-L levels in OUs 3 through 5. While size separation may not in all cases be a cost-effective (or necessary) action, **Case Study 6** shows how one can evaluate if a different (and possibly separable) form of a COPC is a major, minor, or equivalent contributor to SQG exceedance and, possibly, risk. The nature of these coarse-grained fractions, along with biological and flux assays, may help determine whether this Pb poses a risk if left in place, if exceedance above regional reference levels is a management priority.

Characterization of the contaminant distribution in sediment size fractions for organic COPCs can also lend insight into potential contaminant dispersion and behavior, suggest sources of contamination, and provide a general level of insight into sediment assessment and management that is not available with the standard methods of assessment ([Charts 7-8, Appendix B](#)). In **Case Study 7**, the size fraction distribution of PAHs was determined for sediments collected from six OUs at the site. The results for each size fraction was plotted to represent the tPAH contamination that each size fraction contributed to the entire OU. The data were derived by considering the tPAH concentration of the fraction and its mass contribution to the entire OU. At this site, most contaminants reside in the fine-grain fractions (<0.063 mm), a feature that is expected when considering the fines-associated nature of organic contaminants and the generally greater mass contribution of this size fraction to the whole unit. Of interest, however, is the bimodal distribution exhibited for each OU. A significant portion of the tPAH resides in the 1.00- to 0.125-mm fractions, suggesting possible association with coarse-grained organic-rich particles such as wood chips. Of particular interest are the elevated concentrations of PAHs in the outfall corners, OUs 1 and 2, relative to the other units and the dominance of the lighter PAHs in OUs 1 and 2. The dominance of the lighter PAHs in the OU 2 profile and, to some extent, the OU 1 profile, indicate that the source and historical inputs into these corner OUs differ significantly from the rest of the lagoon and from regional signatures in which low levels of the higher molecular weight PAHs dominate. Because lighter PAHs generally exhibit high rates of weathering and degradation under environmental conditions, elevated levels in these sediments imply that the inputs into the corner OUs may be more recent. At this site, OUs 1 and 2 are distinct in PAH fingerprint and concentration from those that lie adjacent, OUs 3 and 4. The differences in PAH signatures can be viewed as evidence that PAH contaminant input into the corner OUs is confined to those units and has not impacted the surrounding areas.

CASE STUDY 6: METALS LOE

Chart 4: Step 7. Risk Characterization Metals COPC Lines-of-Evidence (LOE)



At this site, evidence of toxicity (Figure 11-1) and bioavailability (Figure 11-2) of Pb to benthic organisms is indicated by the bioassays results (1). Grain size analysis of sediments from the site suggests variability in grain size between different OUs, ranging from 25% to 95% fines. Further examination of the sediments reveals a bimodal distribution of Pb between the coarse- and fine-grained fractions (Figure 11-3, 2 through 4). By plotting the net concentration of Pb in each fraction against various sediment benchmarks (Figure 11-4), one can determine if the contribution of the COPC associated with the coarse fractions causes an exceedance of a particular benchmark (5). In this case, the fines-associated Pb in OUs 1 through 5 alone exceeds regional reference levels. Pb associated with the coarse-grained fraction in OU 1 and OU 2 is also substantial. The Pb associated with the coarse-grain fraction alone in these OUs exceeds all the SQGs. Size separation of coarse from fines in OUs 1 and 2 would lead to reduction of contaminated mass ER-M levels, and to below ER-L levels in OUs 3 through 5. The nature of these coarse-grained fractions, along with biological and flux assays, may help determine whether this Pb poses a risk if left in place, if exceedance above regional reference levels is a management priority (6).

CASE STUDY 6 (continued)

Chart 5: Metals COPC Size Fraction Distribution

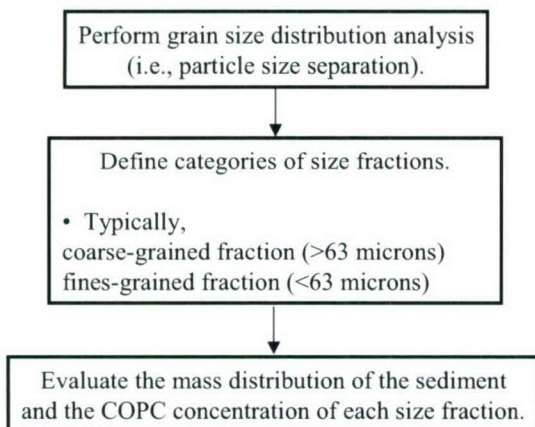


Chart 6: Metals COPC Concentration Contribution of each Size Fraction

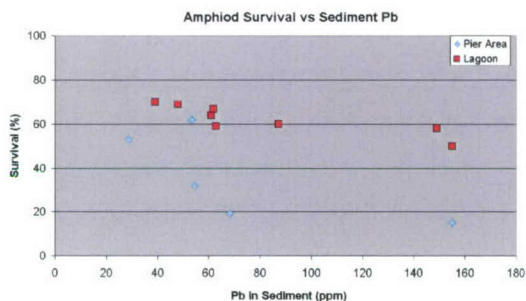
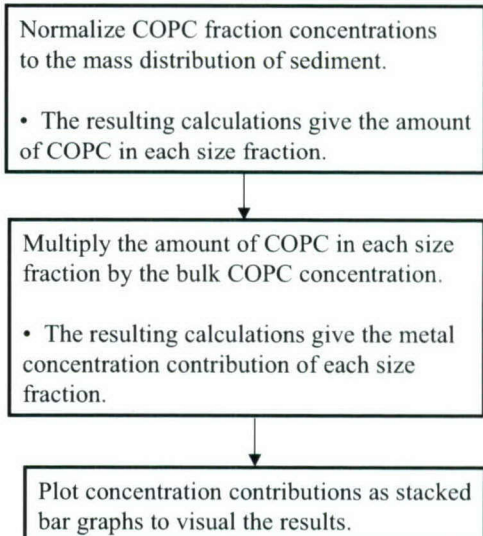


Figure 11-1. Amphipod survival (Pb).

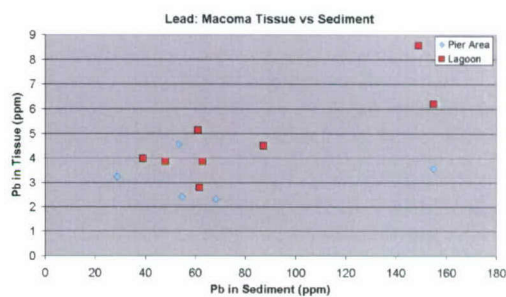


Figure 11-2. Pb in Macoma tissue.

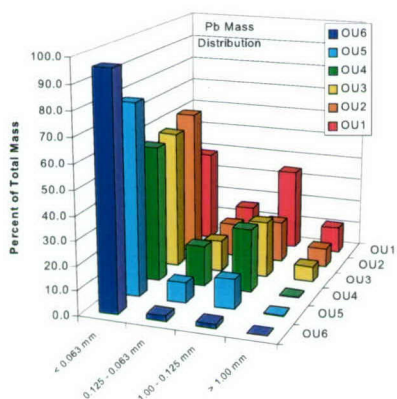


Figure 11-3. Mass distribution of Pb.

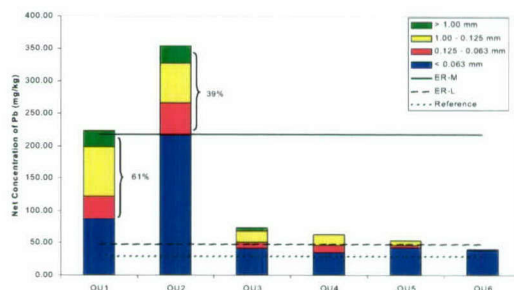
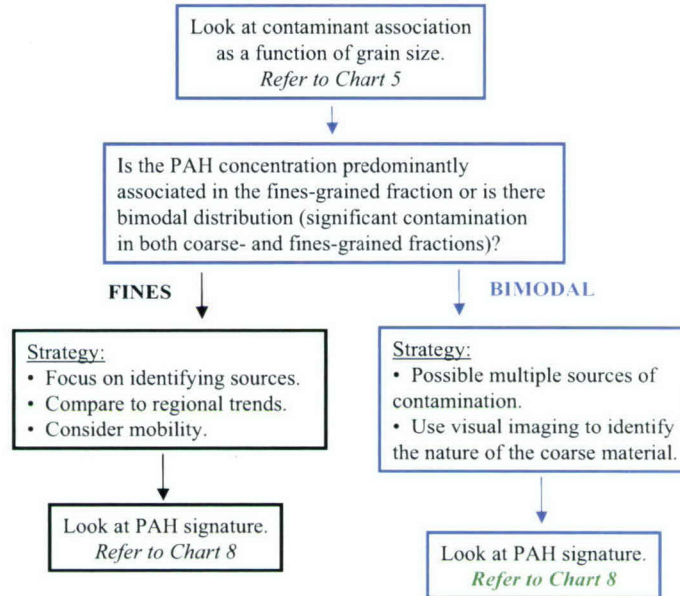


Figure 11-4. Net concentration of Pb.

CASE STUDY 7: ORGANICS LOE

**Chart 7: Step 7. Risk Characterization PAH COPC Lines-of-Evidence (LOE)
(Size Fraction Distribution)**



At this site, the size fraction distribution of total PAHs (Figure 12-1) and individual PAH congeners (Figure 12-2) were determined for sediments collected from six OUs at the site. The results for each size fraction were plotted to represent the tPAH contamination that each size fraction contributed to the entire OU (1). At this site, the most contaminants reside in the fine-grain fractions (<0.063 mm), a feature that is expected when considering the fines-associated nature of organic contaminants and the generally greater mass contribution of this size fraction to the whole unit (2). Of interest, however, is the bimodal distribution that is exhibited for each OU (3). A significant portion of the tPAH resides in the 1.00- to 0.125-mm fractions. Of particular interest are the elevated concentrations of PAHs in the outfall corners, OUs 1 and 2, relative to the other units and the dominance of the lighter PAHs in OUs 1 and 2. The dominance of the lighter PAHs in the OU 2 (Figure 12-3) profile and, to some extent, the OU 1 profile, indicates that the source and historical inputs into these corner OUs differ significantly from the rest of the lagoon and from regional signatures in which low levels of the higher molecular weight PAHs dominate (Figure 12-4) (4). Because lighter PAHs generally exhibit high rates of weathering and degradation under environmental conditions, elevated levels imply that the inputs into the corner OUs may be more recent. At this site, OUs 1 and 2 are distinct in PAH fingerprint and concentration from those that lie adjacent, OUs 3 and 4. This finding is evidence that PAH contaminant input into the corner OUs is confined to those units and has not impacted the surrounding areas.

CASE STUDY 7 (continued)

Chart 8: Step 7. Risk Characterization
PAH COPC Lines-of-Evidence (LOE)
(PAH Site-Specific Signatures)

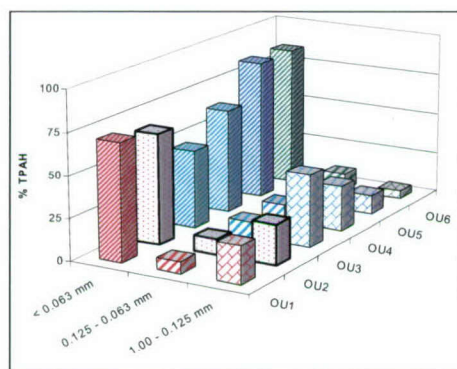
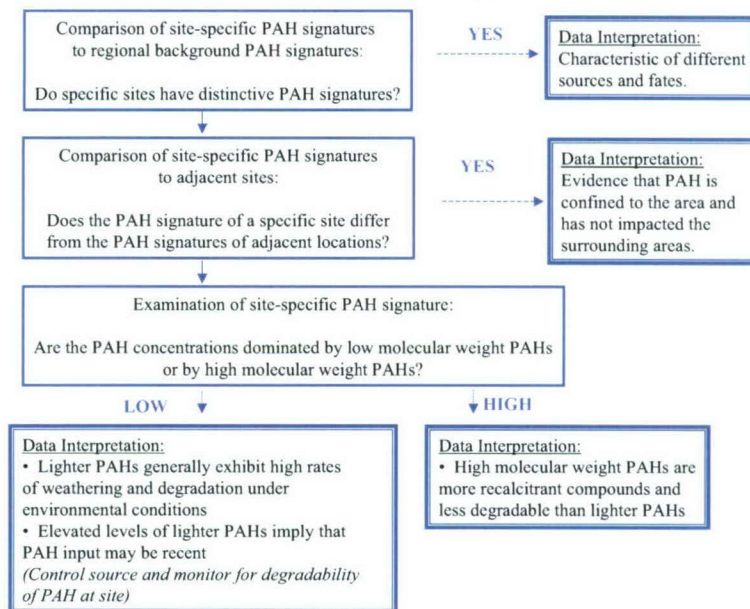


Figure 12-1. tPAH mass contributions.

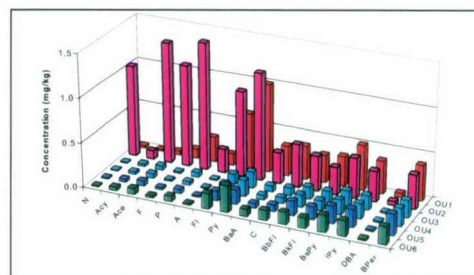


Figure 12-2. PAH distribution (µg/kg), OUs 1 through 6.

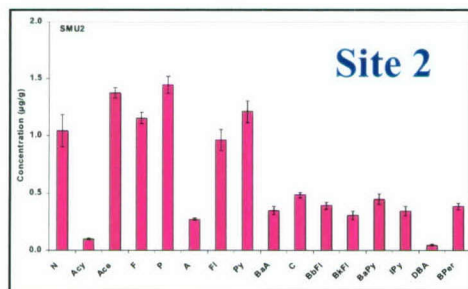


Figure 12-3. OU 2 PAH signature.

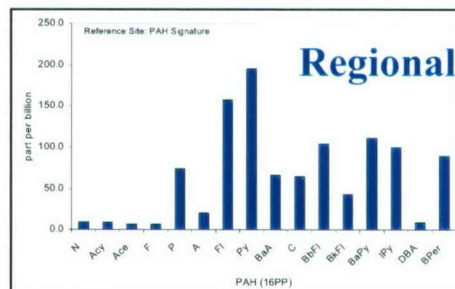


Figure 12-4. Regional PAH signature.

3.5 STEP 8: EVALUATION OF REMEDIAL ALTERNATIVE GOALS (RAGS)

3.5.1 Using Data on Sediment/Contaminant Biogeochemical Signatures to Support Comprehensive Environmental Response, Compensation, and Liability Act Remedy Criteria for Evaluating Remedial Alternatives

When data from the Tier 2 BERA indicate that the site poses unacceptable risk, the next step in the process is the evaluation of remedial alternatives (Tier 3). As remedial alternatives are developed, they are evaluated within the scope of the nine Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) remedy evaluation criteria identified in the National Contingency Plan (NCP) [40 CFR 300.430(e)(9)(iii)] (see textbox below). The main objectives of the Tier 3 evaluation are to evaluate alternative remedies and to support the selection of a preferred remedy. As discussed throughout this report, biogeochemical characterization techniques are useful in addressing these objectives. Links to relevant case studies in this document are provided for each of the principles highlighted below. **Section 4 (Use of Sediment Data in the Evaluation of Remedial Options)** of this report examines the various remedial options in greater detail and illustrates, through the use of many of these case studies, where data on contaminant/sediment geochemical signatures can aid in evaluating these options.

- Threshold Criteria
 1. Overall protectiveness of human health and the environment
 2. Compliance with Applicable or Relevant and Appropriate Requirements (ARARs)
- Primary Balancing Criteria
 3. Long-term protectiveness and permanence
 4. Reduction of toxicity, mobility, or volume through treatment.
 5. Short-term effectiveness
 6. Implementability
 7. Costs
- Modifying Criteria
 8. State acceptance
 9. Community acceptance

3.5.1.1 Long-Term Protectiveness and Permanence

- *“Evaluations of long-term protectiveness and permanence should consider:*
- *Whether COPC input to the site will continue from other sources,*
- *The reliability of institutional or engineering controls in reducing ecological risks,*
- *The residual risks to the assessment endpoints, and*
- *The recovery potential of the impacted habitats.”*

See <http://web.ead.anl.gov/ecorisk/process/pdf/process4.pdf> for discussion of the CERCLA Remedy Evaluation Criteria).

A key component of this criterion is evaluating the magnitude of the residual risks that remain after selecting a remedial action. The amount of residual risk from Monitored Natural Recovery (MNR) depends on the degree of long-term sedimentation/burial by clean sediments or contaminant weathering/biodegradation that occurs at the site. The evaluation of surface and core data can be used to determine whether consistent sediment deposition is occurring at the site with a high rate of burial (**see Section 3.3.1 for discussion**). Mass distribution and COPC fingerprints (e.g., congener histograms) illustrate the potential of contaminant weathering or biodegradation in reducing residual risk at a site (**see Case Study 7, Section 3.4; Case Study 10, Section 4.3**).

Evaluating the contaminant distribution as a function of grain size is useful in determining the risk of residual contamination that may occur during remedial dredging. For instance, a site may contain highly contaminated fine-grained sediments. Because fine-grained sediments can be the most mobile when resuspended, this fact should be considered in an evaluation of the potential residual risks of dredging.

Contaminant source control is also an important aspect of ensuring the long-term permanence of any remedial action. After outside sources have been identified and controlled, efforts should be made to determine if the sediments are a major source of contamination. Again, understanding contaminant distribution and mass balance can help in making decisions regarding the potential for sediments to act as a continued source of contamination to the environment (**see Case Study 9, Section 4.3**).

3.5.1.2 Reduction of Toxicity, Mobility, or Volume through Treatment

"Evaluations of toxicity, mobility, or volume reduction should consider:

- *Whether the remedy will reduce toxicity sufficiently to bring risks to acceptable levels, and*
- *Whether the remedy will reduce the likelihood of the contaminants migrating to other habitats (both on- and off-site) currently not at risk."*

Evaluating COPCs in terms of mass distribution, COPC fingerprint (e.g., congener histograms), contaminant distribution as a function of grain size, etc., provide information in determining the reduction of toxicity created by a selected remedial action. For instance, the reduction of toxicity from biodegradation should be considered in cases where degradable compounds represent a significant portion of the risk (**see Case Study 10, Section 4.3**).

Examination of the grain-size contaminant distribution of sediments is useful in determining the probability that the remedial action will reduce contaminant migration. Fine-grained sediments are often very mobile when resuspended. If these sediments are at the surface, contaminant mobility is a risk if sediments are left in place. If these highly contaminated sediments are buried under clean sediment, contaminant mobility is a risk if sediments are dredged (**see Case Study 9, Section 4.3**).

Volume minimization/reduction should be investigated in sites where contaminants are highly correlated with sediment grain size. In such cases, size separation of sediment may reduce the volume of sediment in need of remedial action and minimize treatment costs (**see Case Study 11, Section 4.6**).

3.5.1.3 Short-Term Effectiveness

“The evaluation of short-term effectiveness should consider:

- *The ecological impacts expected with implementation, together with the effectiveness and reliability of associated mitigation measures, and*
- *Whether the impacted habitats will recover in a “short” time period.”*

This criterion evaluates the effects of constructing and implementing the selected remedial action until remedial goals are achieved. The biogeochemical techniques (evaluating COPCs in terms of mass distribution, COPC fingerprint, contaminant distribution as a function of grain size, etc.) discussed in the previous criterion can provide data to address the short-term effectiveness of the selected remedy.

3.5.1.4 Costs

“Although the relationship between the BERA and evaluations of remedy costs may not be immediately obvious, large cost differences may be associated with different levels of risk reduction.”

“Thus, Tier 3 should evaluate the consequences to overall remediation costs of different risk reduction levels.”

Biogeochemical characteristics techniques focus on delineating distinct operating units of sediment in need of remedial actions (see **Case Study 5, Section 3.2.2**). Evaluating the quantity and nature of contaminated sediments within the different operating units can provide an improved assessment of the cost of the selected remedy. For instance, a site may consist of high concentrations of COPCs covering small discrete areas. The mass distribution of contaminants within this site’s OUs may reveal that remedial actions in those discrete areas significantly reduce risk levels (see **Case Study 8, Section 4.1**). Large cost differences may be realized by focusing the selected remedy within the areas of large risks.

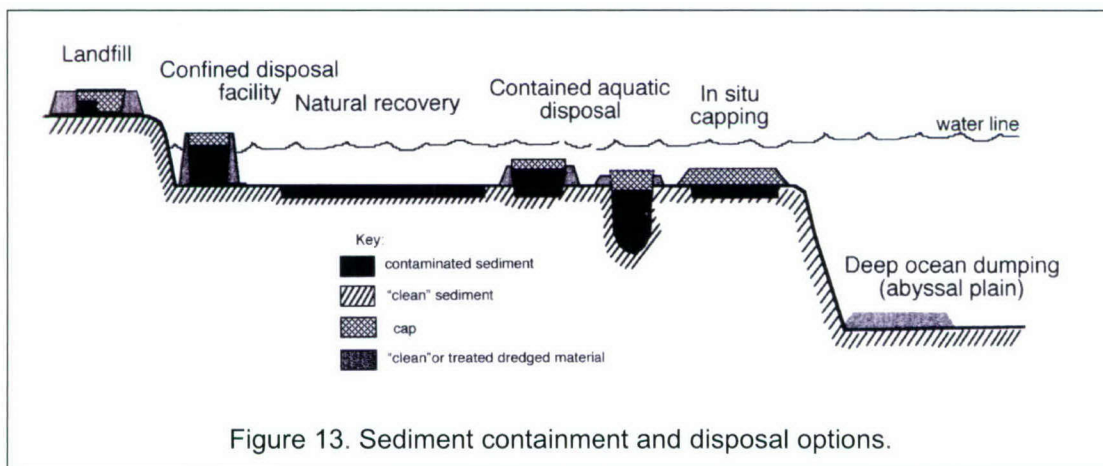
Size fraction information can also be used to compare cost estimates between various remedial actions. For instance, particle separation for volume minimization can be cost-effective if it is determined that the bulk of contaminant resides in a separable sediment fraction that is a relatively small portion of the total sediment volume. Cost-savings evaluations can be made comparing the pre-treatment costs of particle separation with the disposal costs associated with large-scale dredging (see **Case Study 11, Section 4.6**).

4. USE OF SEDIMENT DATA IN EVALUATION OF REMEDIAL OPTIONS

Sediment management strategies fall into five broad categories that are selected based on an evaluation of site-specific risks and goals: (1) no further action (NFA), which is only appropriately applied if it is determined that sediments pose no risk; (2) monitored natural recovery (MNR), based on the assumption that while sediments pose some risk, it is low enough that natural processes can reduce risk over time in a reasonably safe manner; (3) in situ containment (ISC) in which sediment contaminants are in some manner isolated from target organisms, though the sediments are left in place; (4) in situ treatment (IST); and (5) removal via dredging or excavation (followed by ex situ treatment, disposal, and/or reuse). **Figure 13** (from NRC, 1997) illustrates various sediment containment and disposal scenarios from in situ to ex situ. The information required to evaluate or compare each of these options is fundamentally different, and any assessment should be designed to evaluate and support management goals and potential remedial options. Because U.S. EPA guidelines suggest that "All remedies that may potentially meet the removal or remedial action objectives...should be evaluated prior to selecting the remedy" (OSWER, 2002), careful planning is necessary to ensure that sampling and analysis plans are designed so they can address these disparate needs in a meaningful and comparable way.

For a summary of the advantages, disadvantages, costs, and maturity of various existing and innovative sediment remedial technologies, see Table 4-6 in the "Implementation Guide for Assessing and Managing Contaminated Sediment at Navy Facilities" (Naval Facilities Engineering Command, 2003) and its references. This guidance illustrates how site-specific sediment/contaminant distribution data can be used to help evaluate the potential risks and benefits of various remedial options.

To evaluate these, sediment quality and risk must be compared to target environments. If removal is a given, in-place risk is irrelevant. If removal is evaluated, then risk and transport in various environments must be predicted (from NRC, 1997).



Because sediments throughout a region of interest may differ in risk, type, distribution, and degree of contamination, hydrodynamics, sediment type, etc., sediments are managed as OUs (see **section 3.3.1 for discussion**). Thus, to appropriately manage a site, strategies are selected for each OU, and a large site or region may apply many management strategies. One must consider the combined effects of these various strategies on the overall health of a region. In the short term, management strategies applied on one OU may have beneficial or detrimental effects on the health of related OUs (for example, dredging in one area may cause resuspension and contamination of another unit or it may reduce the risk of such dispersion). To be successful, management objectives must be determined, and the long-term impact on the ecological health of a region must be considered.

4.1 Using Site Data to Evaluate Costs and Benefits of Management Objectives

An important part of management option selection is the evaluation of management goals, whether they are cleanup levels, remedial action objectives (RAOs), measurement endpoints, or ecological goals. Not all approaches can achieve all goals, and an evaluation of site-specific characteristics may help frame the costs, benefits, and feasibility of various approaches and objectives. One approach to evaluating these issues is to examine the distribution of contaminants in various regional OUs relative to each other and various potential benchmarks and criteria. **Case Study 8** illustrates some examples. In this case study, a contaminated site is examined as a given volume of sediment (with established borders and depth of concern) so that a mass balance of COPCs, as a function of potential OUs, can be examined. **SOP 1** illustrates numerical approaches to this issue. The site of concern is divided into five OUs (based on contaminant distributions, see **Case Study 5, Section 3.2.2**). In this case, sediment COPC levels were determined from composited samples from each OU. Other approaches are to generate average compositions from core and/or depth data (see **SOP 1, steps 1-3; Appendix A**), but in all cases, it is the average COPC concentration in an OU that is determined here. These calculations provide average COPC concentrations in each OU sediment volume. While contaminant concentration throughout a site may be mapped in many ways throughout a study (e.g., distribution of surface concentration, etc.), this examination of average COPC concentration within a sediment unit is important here because it is units of sediment, not individual cores or grabs, that will be subject to selected management strategies. Thus, rather than letting small hot-spots based on single fliers drive the evaluation of OUs (see **Section 3.2.2 for a discussion of detection frequency evaluation**), weighted averages for OU contaminant levels allow for a more reasoned comparison of volumes of sediment to be managed. **Figure 14-1** shows the concentrations of organic COPCs in the OUs. Clearly, OUs 1 and 2 have the highest concentrations of the organic COPCs. This finding would suggest that these units, which have high levels relative to the other OUs and relative to a number of SQGs, are of potential concern. If this site has reached the point where management options are considered, then clearly, the ERA ruled out NFA.

While absolute concentrations of COPCs in sediments are an important part of assessing site sediments, for many reasons, absolute concentrations do not provide a full picture of what is going on at the site. Risk management may be approached from several angles, and contaminant concentrations are only one aspect of risk management. It is also important to evaluate relative and absolute loading of contaminants in a region. What actual amount of a COPC is in an area? How is it distributed? What is the potential impact to total loading if given sediment volumes are contained, controlled, or removed? The next step, described

below, is to examine the distribution of contaminant mass within a region of concern as a function of OU. SOP 1 describes the numerical approach. **Figure 14-2** shows the absolute distribution of sediment and contaminant mass in OUs of the region. The first thing to note is that the bulk of sediment mass lies in OUs 3 through 5, with only 8% of the total mass lying in OUs 1 and 2. Mass (kg) of contaminant in a given OU can be divided by the total contaminant mass in Seaplane Lagoon (sum of the OUs) to determine which units account for the bulk of contaminant loadings in the region. Because PCBs are ubiquitous, the large volumes of sediment in OUs 3 through 5 offset the high concentrations in OUs 1 and 2. For DDTs and PAHs, concentrations in OU 2 are so high that the unit dominates the mass loading. Thus, if the management goal is a net removal or containment of COPC mass, these distributions raise interesting points. Roughly $\frac{3}{4}$ of the tPAH and tDDT in the region could be removed or contained by dredging or capping OUs 1 and 2 (8% of the sediment volume). This action would, however, only contain or remove about 42% of the tPCBs (**Figure 14-3**).

Organic and inorganic contaminants can exist in a region at background, ambient, or natural levels, either because they have natural sources or because entire regions in urbanized, industrialized, and other areas are exposed to ubiquitous levels of anthropogenic input. In many cases, because such contaminants tend to associate with fine-grained sediments, a general regional tendency is to have a “mixing curve” of contaminated fines, and relatively uncontaminated coarse-grained sediments. In such a case, a COPC in sediments can be plotted versus a metal indicative of fine-grained minerals (e.g., Fe or Al), percent fines, or, in some cases, percent organic carbon. With such an approach, sediments that fall along an ambient trend are distinct from those that have a unique source of contamination. While ambient or background levels of COPCs can be bioavailable, and may cause ecological impact, they are almost impossible to manage on a site-specific basis—cost and logistics make it improbable that an entire region will be remediated, and if specific sites are remediated to below ambient levels, those sediments are probably subject to re-contamination by background sediments. Thus, it is important at a given site to examine contaminant distribution relative to regional ambient or background levels (how are contaminants that may be controllable or site-specific distributed?)

While absolute concentrations of a given COPC are important to know, another useful tool is to examine the distribution of contaminants in sediments that exceed chosen SQGs (see **Section 2.4 for a discussion of SQGs**). What SQGs are appropriate at a given site depends on the risk models used, the priorities of the stakeholders involved, and the questions asked of the sediment. In this case study, we discuss COPC distributions in the OUs relative to regional reference levels and ER-M levels (Long et al., 1995). Another approach that can be applied is not to compare sediment to SQGs, but rather to generate site-specific benchmark values based on site chemistry and bioassay results. Contaminant levels in sediments at the site can be compared with toxicity assays, bioaccumulation, or flux measurements in the same sediments. If correlations are observed, “acceptable” contaminant levels can be selected for the site. **SOP 1** (Step 7) illustrates the numerical approach for evaluating the amount of COPC in each OU that exceeds selected benchmarks, whether they are regional reference values or selected SQGs. In **Figure 14-4**, pie charts compare the distribution of tPCBs in sediments in two ways: absolute COPC mass distribution, and distribution of COPC exceeding ER-M. For PCBs, if the management goal is to remove absolute PCB mass, or all sediments exceeding regional reference levels, large volumes of sediment must be removed

or contained. If the goal is to manage sediments exceeding ER-M⁸, then only OU 1 and OU 2 need active management. While this approach may be a reasonable choice, if resources are unlimited, it is important to use site-specific data to balance resources with ecological benefit. In many cases, many more potential OUs and much larger volumes may exist. If management goals are set at too restrictive a threshold such that remedial costs become prohibitive, they may never be implemented. It is thus important to examine the volume and cost implications of various benchmarks (meaningful to the site) to maximize ecological benefits with potentially limited resources.

In the same way that contaminant distribution within sediment fraction was used to provide insight into possible contaminant sources, contaminant distribution within volumes of sediment can provide insight into how achievable various management objectives may be, and what management strategies should be considered. In **Case Study 8**, the same procedures described above were used, but PAHs were broken into different categories. Many organic COPCs are reported as sums of classes (e.g., tPAH, tPCB, etc.) rather than as individual molecules. While this approach allows for some compression of potentially vast amounts of data, it buries a significant amount of information about the characteristics of contaminant classes within a region. A review of site data shows that different OUs have distinct PAH signatures. OUs 1 and 2 have PAH distributions with a much higher proportion of the lighter, more biodegradable PAHs, while the other OUs have PAH signatures dominated by the heavier, more recalcitrant PAHs. If one is interested in evaluating potential behavior of PAHs in the region, then tPAH alone does not provide the complete picture. Instead, PAHs can be broken into subcategories (**see Section 2.5 for a more detailed description of these sub-categories**): total PAHs (tPAH), low molecular weight PAHs (LMWPAH), and high molecular PAHs (HMWPAH).

The relative distribution of the LMWPAHs (**Figure 14-5b**) strongly affects the tPAH distribution (**Figure 14-5a**) because LMWPAHs are a major component of the high concentrations observed in OU 1 and OU 2 (**Figure 14-5c**).

⁸ It is not the intent of this report to suggest that these are the criteria that should be applied to a site for assessment or management purposes. Rather, we have selected these as examples to demonstrate how data can be manipulated to frame and address questions at the site. Risk managers can apply any regional levels or SQGs that are appropriate, using the approach described.

CASE STUDY 8: INTERPRETING CONTAMINANT MASS DISTRIBUTION

Management strategies are often dictated by management goals. Knowing the average concentration of contaminants in an OU sediment volume as well as the mass distribution of contaminants in that sediment volume are important for remedy selection. How one examines and interprets contaminant mass distribution depends on what aspect is important for the question at hand. If managing sediments exceeding a given contaminant concentration is a goal, a simple evaluation of contaminant concentration in each OU will be important (Figure 14-1). In this case, OUs 1 and 2 has the highest concentration of organic constituents.

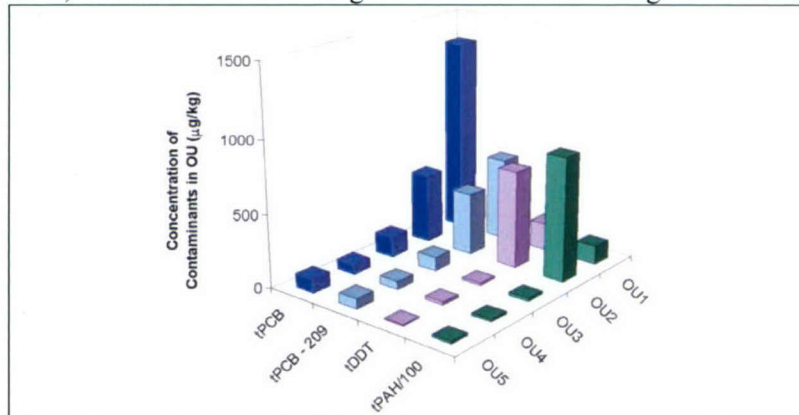


Figure 14-1. Evaluation of contaminant concentration for organic constituents.

If reducing absolute contaminant loads is a goal, determining which sediment units account for the bulk of the contaminant loadings at the site will be important. This can be accomplished by dividing the mass (kg) of contaminant in a given OU by the total contaminant mass at the site (sum of OUs) (Figure 14-2). Because PCBs are ubiquitous, the large volumes of sediment in OUs 3 through 5 offset the high concentrations in OUs 1 and 2. For DDTs and PAHs, concentrations in OU2 are so high that the unit dominates the mass loading.

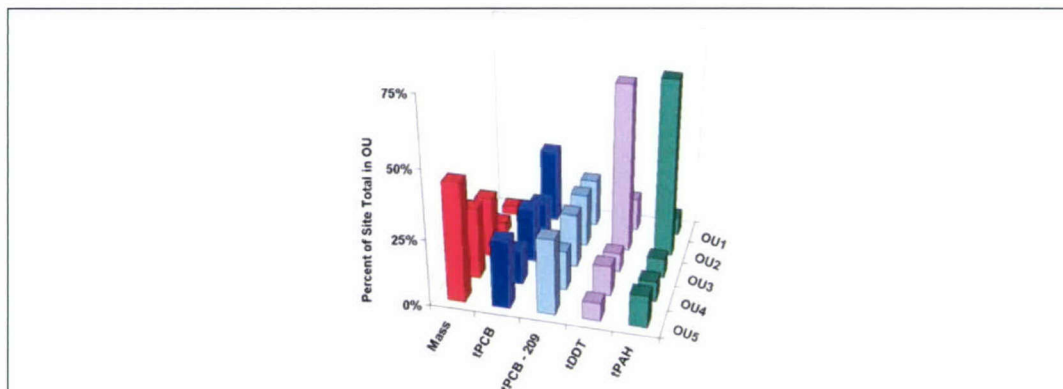


Figure 14-2. Evaluation of contaminant mass loading.

CASE STUDY 8 (continued)

It is also important to evaluate relative and absolute loading of contaminants in a region. Questions such as “what is the actual amount of COPC in an area, how is it distributed, and what is the potential impact to total loading if given sediment volumes are contained, controlled or removed?” are important to addressing risk management issues. Figure 14-3 provides such an example.

	OU1	OU2	OU3	OU4	OU5	OU 1+2
Sediment Mass	3	5	22	29	41	8
tPAH	7	66	7	8	12	73
tPAH ex. ERM	0	100	0	0	0	100
tPAH ex. RR	7	93	0	0	0	100
tDDT	12	63	7	11	7	75
tDDT ex. ERM	13	87	0	0	0	100
tDDT ex. RR	14	86	0	0	0	100
tPCB	28	14	20	13	25	42
tPCB ex. ERM	73	27	0	0	0	100
tPCB ex. RR	29	15	20	12	24	44

ERM: Effects Range-Medium	RR: Regional Reference Levels
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Goal: Net removal/containment of contaminant mass.	Question: How are contaminants distributed and how much volume must be removed to meet this goal?	Answer: By removing/containing OUs 1 & 2 (8% of sediment volume), ~ 75% of tPAH and tDDT will be removed. However, only 42% of tPCB will be removed.
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Figure 14-3. Contaminant loading.

Examination of the contaminant distribution in sediments in exceedance of selected benchmarks is another useful way in which data can be used to evaluate different management options. Figure 14-4 provides an example.

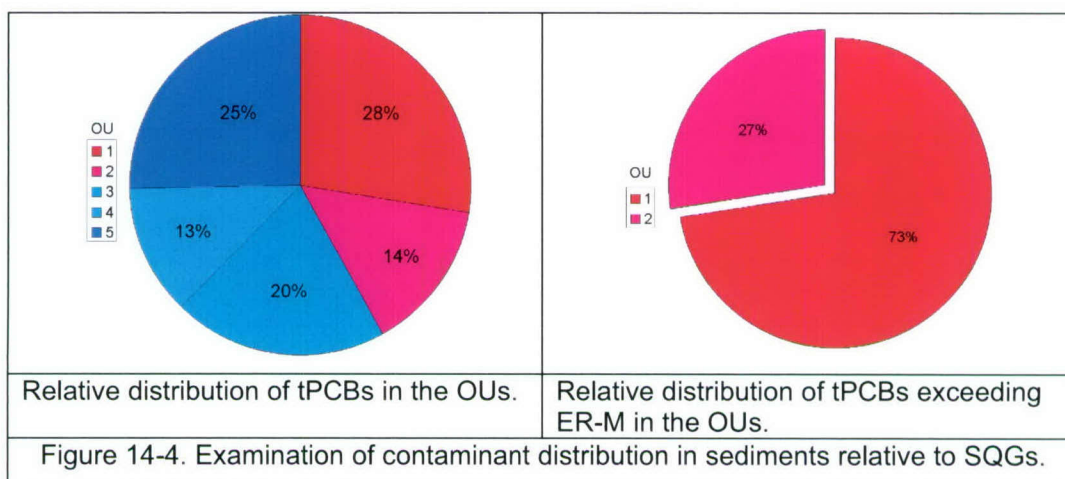


Figure 14-4. Examination of contaminant distribution in sediments relative to SQGs.

CASE STUDY 8 (continued)

By looking more closely at the characteristics of a particular contaminant class, information can be obtained that can also help in evaluating different remedial options. For example, for contaminants such as PAHs, information regarding the mass of the degradable fraction (light-weight PAHs), the recalcitrant fraction (heavy weight) or total mass loading might be relevant in determining whether monitored natural attenuation (biodegradation) might be a feasible option. In Figures 14-5a through 14-5d, a large proportion of the total PAHs are in OU 2 and are predominantly low molecular weight PAHs (more biodegradable), while the more recalcitrant heavy molecular weight PAHs are ubiquitous throughout the lagoon. Thus, if PAHs were a risk driver at the site, eventual natural attenuation by biodegradation could be considered in the site management plan.

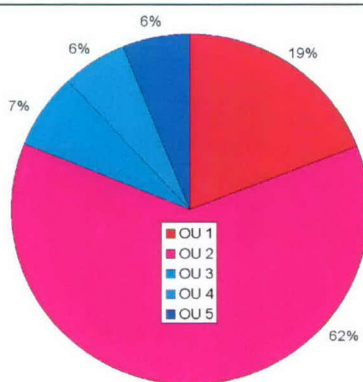


Figure 14-5a. Relative mass distribution of total PAHs in OUs.

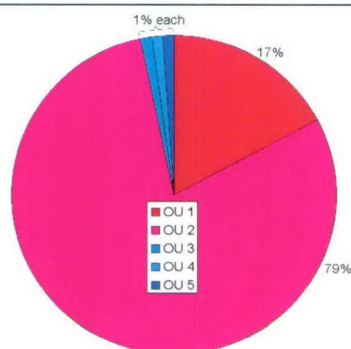


Figure 14-5b. Relative mass distribution of LMWPAHs in OUs.

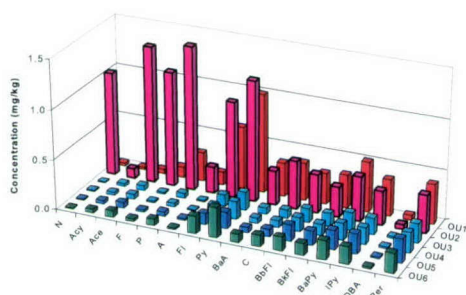


Figure 14-5c. PAH distributions in sediment units at the site suggest that different units have distinct source signatures. OU 2 stands out with light PAHs dominating (indicative of "fresh" material).

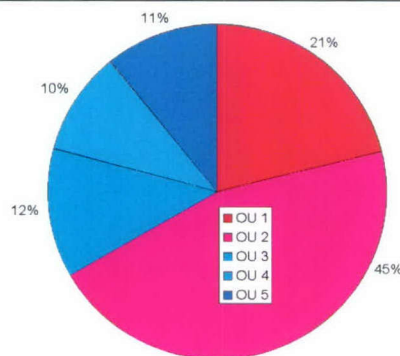


Figure 14-5d. Relative mass distribution of HMWPAHs in OUs.

The HMWPAHs (**Figure 14-5d**), which follow more along the line of the mass distribution, do not appear to significantly influence the tPAH distribution and, thus, are not particularly enriched in the corner OUs. From a risk management perspective, one can see that large HMWPAHs (**Figure 14-5d**), which follow more along the line of the mass distribution, do not appear to significantly influence the tPAH distribution and, thus, are not particularly enriched in the corner OUs. From a risk management perspective, a large portion of the PAHs in the region appear mostly in OU 2 are probably biodegradable, while the more recalcitrant HMWPAH compounds are ubiquitous throughout the lagoon. Thus, if PAHs were a risk or decision driver at the site, eventual natural attenuation by biodegradation could be considered in a site management plan. However, because the same OUs with biodegradable PAHs are enriched with less degradable PCBs and non-degradable metals, bioremediation, whether natural or engineered, is probably not a reasonable management approach at this site.

4.2 NFA

As stated above, the selection of NFA is based on the assumption that risk is so low that no management tasks are necessary. This situation occurs when a risk assessment reaches a point at which exit criteria are met, and a site or unit poses little or no risk. If a risk is thought to exist, but due to background considerations (such as a ubiquitous regional input) the risk is not easily manageable, then source control, monitoring, and, ideally, recovery over time, will be the management strategy. Such an approach is a subset of MNR rather than NFA.

4.3 MNR⁹

In some situations, the large volume of sediment to be remediated, low risk of in-place contaminants, poor feasibility, or high risk of removal and/or the associated costs may lead the decision-maker to select an MNR option. MNR of sediments as a remedial option relies on natural environmental processes to permanently reduce risk and requires careful assessment, modeling, and monitoring (see also Swidoll, Staj, and Ells, 2000). Pertinent natural processes often associated with this remedy, discussed below, include sediment deposition (burial), dispersion, mixing, irreversible adsorption, and chemical and biological reactions. MNR differs from NFA in that assessment, modeling, and long-term monitoring are required to verify that recovery is taking place, while the selection of NFA is generally based on the assumption that risk is so low that these tasks are not necessary. An important component in a successful MNR (as with most management strategies) is the aggressive implementation of source controls (**see Section 1.9.2 for discussions of the use of sediment data to evaluate potential contaminant sources**).

The selection of MNR is predicated on an evaluation of the risks and costs of leaving sediments in place and the risks and costs of removing and/or treating them. Given that a site possesses appropriate conditions, benefits of MNR may include reduction or elimination of secondary impact on habitats caused by dredging or construction, lower risk to workers, avoidance of possible resuspension, avoidance of disposal requirements, and lower potential cost than more invasive remedies. Because MNR is potentially a long-term approach and monitoring times and costs can be significant, objectives must be clear and backup plans should be in place if risks increase or fail to decrease over time.

⁹ While this section draws heavily from Apitz et al., 2002, this guidance has been significantly modified. Though much of this section does not focus on sediment/contaminant geochemical signatures, because MNR is a sufficiently important emerging sediment management strategy, it was thought that a broad discussion would help this guidance.

This section provides tables of assessment tools for evaluating the potential for MNR, broken into three categories: (1) sedimentation/burial by clean sediments, (2) contaminant weathering and biotransformation/degradation, and (3) ecological recovery. This section also briefly discusses modeling. A reliable site conceptual model is needed, which is a qualitative or quantitative statement and diagram of how the various physical, chemical, and biological processes affect risk. For more complex sites, many mathematical models are available, including those that focus on hydraulic, sediment transport, physical and chemical transport, and biological/ecological processes. They are generally applied in sequence, the outputs of the more basic models becoming the inputs to the more advanced. The major purpose of this report, however, is to illustrate how one uses data on contaminant distributions and interactions in sediments to frame decisions. To that end, simplified examples, rather than complex, multivariate models, are used in the discussion.

When assessing a site for the potential for MNR, it is also important to identify parameters that are counter-indicative. These parameters include ongoing contaminant sources, immediate and significant harm to human health or the environment, insufficient deposition of clean sediments, ongoing or potential high-energy resuspension, low sediment sorptive capacity, microbial processes that enhance bioavailability, and instances where active remediation can achieve risk-based objectives more rapidly. MNR should always be assessed in comparison with other remedial alternatives, and should encompass beginning-to-end risks.

Generally, monitoring required by regulators for MNR will be more rigorous than those associated with other remedial alternatives, and the duration of monitoring will probably exceed other alternatives. By definition, MNR is a risk management strategy. The most fundamental applicability requirement for MNR is that the RAOs must be risk-based. If COPC mass removal is required for reasons other than risk reduction, MNR will not fulfill that requirement. Use of MNR as a protective alternative is based on the assumption that the risk posed by a contaminant is closely associated with its spatial and temporal proximity to receptors, and that natural processes can function to eliminate or limit that proximity. In most cases (barring degradation), contaminants remain in the environment, though sequestered from the biota. While this fact can be unsettling for many parties, many other remedial strategies (barring those that achieve destruction of contaminants) also work by isolating or removing contaminants from the food chain, but often by moving them to other environments (e.g., Contained Disposal Facilities [CDFs], landfills, etc.). The fundamental assumption behind MNR is that the risk posed by a contaminant is controlled by its spatial and temporal proximity to receptors, and those natural processes can function to eliminate or limit that proximity. Acceptance of these approaches also presumes the long-term stability of this isolation.

Natural recovery processes play an important role in any remedial action by reducing margin risks and repairing unavoidable damage of more invasive alternatives. The object of the remedial alternative assessment for MNR is to weigh its advantages as a primary alternative against other combinations of alternatives, which ultimately include natural recovery as a "polishing step," or which include natural recovery for the less contaminated margins. Another important assessment function, including measurements and modeling, is to help quantify and compare the potential effectiveness of clean sediment layers in isolating contaminants versus the possible effects of rare erosive events such as storms.

The application of MNR as a remedial alternative for sediments is not as well understood or studied as MNA is in its application to groundwater¹⁰. However, many physical-chemical-biological parameters can be considered. Selection of MNR is largely based on identifying in situ factors controlling the fraction of the COPC that is bioavailable to the sensitive receptor group(s). Sensitive receptor groups and the natural processes that either ameliorate or exacerbate the exposure of these organisms to the COPC are specific to the contaminant in question and the site. Consequently, success of MNR as a remedial strategy depends on an accurate and specific understanding of the contaminated environment and, thus, the site-specific conditions that control the dynamics (risk mechanism, fate, and mobility) of the COPC in that environment.

Many contaminated marine sediment sites under investigation are in shallow coastal areas. These sites are much more likely than more traditionally studied offshore sediments to be impacted by advective processes such as groundwater flow, tidal and wave pumping, and resuspension via ship and storm activity. While these processes are recognized in the oceanographic community as having significance to chemical fluxes, they are largely unstudied in contaminated systems. The relative magnitudes of these processes as compared to the traditionally assessed processes such as diffusion and bioturbation have not been determined. These issues must be addressed for near-shore sediments. If impacted sediments are to be left in place, it is critical to evaluate potential pathways by which contaminants might pose an ecological or human health risk, and to monitor, minimize, or eliminate these pathways. On the other hand, the relative importance of these pathways as mechanisms of sediment recovery must also be determined. While the EPA and others are turning towards an evaluation of the appropriateness and efficacy of in-place management strategies, as yet, the understanding of the relative importance of transport pathways (e.g., diffusive versus advective, etc.) is only qualitative and difficult to apply in a management selection or evaluation, whether using MNR or more aggressive approaches.

At all sites where MNR is considered a possible management strategy for contaminated sediments, identification of the source of the COPC is crucial. Physical processes that support MNR by sequestration of the COPCs deep in the sediment (e.g., burial with clean sediment) are dependent on developing a relatively contaminant-free physical barrier between contaminated sediments and sediments in contact with the sensitive receptors within the infaunal, benthic, and pelagic communities. Within contaminated sediments, the microbial processes catalyzing the transformation and/or mineralization of the COPC can be slow and are often constrained spatially and/or temporally. For these reasons, MNR as a remedial strategy is generally incompatible with a continuing input (i.e., point sources) of fresh contaminant. However, for biodegradable contaminants such as some PAHs, growing evidence shows that sediment microbial communities can adapt to degrade ongoing inputs (e.g., Montgomery et al., 1999). The rates and extent of these processes in the field are the subject of ongoing research, some of which will be discussed below.

Successful use of MNR to manage risk associated with contaminated sediments requires an understanding of the specific natural processes acting in the environment that affect the fate, mobility, and availability of the COPC. Once the source of contaminant has been eliminated, management of contaminated sediments using an MNR strategy is largely a matter of limiting flux of the COPC out of the sediment and limiting the mobility of the contaminated

¹⁰ Science Advisory Board (SAB). 2000. "Review of EPA's Natural Attenuation Research Program." First Draft Report to Carol Browner, Administrator, Environmental Protection Agency, 2 August.

sediments. As such, many interacting physical, chemical, and biological processes contribute to natural recovery in sediments. Burial and sequestration of the contaminated sediments under a fresh layer of clean sediment often limit the bioavailability of the COPC. For instance, in sediments from Lavaca Bay, Texas, total mercury extends deeper into the sediment than methylmercury, suggesting that the buried total mercury is less available for mobilization through microbial methylation than mercury closer to the sediment/water interface (Gill et al., 1999). Additionally, Frazier et al. (2000) suggest that gradual burial of mercury-contaminated sediments in Fairhaven Bay and Sudbury River (Massachusetts) reservoirs has reduced the amount of mercury available for methylation in these sites. If burial of the COPC is anticipated as an aspect of MNR for the site, it will be important to determine if the environment has a source of clean sediments adequate to cover and protect the contaminated sediment layer. Hydraulic characteristics of the environment that limit the resuspension and transport of the sediments will also contribute to minimizing the mobility of the COPC in the environment.

While mechanical/physical processes limit the bulk movement of the contaminated sediments in the environment, chemical and biological processes will be the most important in determining the mobility and bioavailability of the COPC itself. For example, sediment mixing associated with the activities of sediment dwelling organisms (bioturbation) can significantly impact the interfacial transport processes. Surface characteristics and the organic content of the sediment substrate will affect partitioning of the COPC between the porewater (available for flux out of the sediment) and the sediment as well as the reversibility of the binding of the COPC to the sediment. Partitioning processes often lead to the sequestration of chemicals in inaccessible microsites or as residues covalently coupled to the organic fraction of the sediment particles. This binding often reduces the overall bioavailability, toxicity, and bioaccumulation potential of the contaminant. For example, chloroanilines have been shown to react and bind with sediments as demonstrated by their resistance to subsequent extraction with solvents. These strong interactions are probably the outcome of covalent bonding between the amino groups and the oxygen-containing group of the humic fraction of the sediment (Beyerle-Pfnur and Lay, 1990). Significant research is underway to evaluate the "irreversible" sorption of contaminants on sediments. Many methodologies have demonstrated that not all contaminants in sediment are easily leachable, degradable, or bioavailable. What is not clearly understood is whether this binding limits bioavailability for all organisms, some of which may interact with sediments in entirely different ways (e.g., surface contact, ingestion, burrowing, etc.). A further discussion of bioavailability is available at the following Web site: <http://www.sediments.org/sedmgt.pdf>.

The surface characteristics, redox potential, pH, and chemistry of the sediments are also important determinants of the speciation of the COPC and will influence the partitioning of contaminants between the solid and aqueous phases of the sediment. For example, toxicity of metals is often related to their interstitial porewater concentrations rather than total mass in sediments. In many sediments, the concentration of acid-volatile sulfide (AVS) is the key factor in determining interstitial water-metal concentrations because AVS/metals form insoluble sulfide complexes with minimal biological activity (Ankley, 1996). However, the stability of these sulfides is contingent on sediments remaining reduced; aeration due to mixing and resuspension, bioturbation, or bioirrigation may affect metal availability on unknown time and space scales.

Microbial processes can support the goals of MNR in sediments in many ways. For example, the in situ biological degradation of hexachlorobenzene (HCB) occurs over

16 years in the anaerobic sediments from a lake in the Netherlands. The reported half-life for HCB was ~7 years and HCB degradation was biologically mediated because of a concomitant increase in di- and tri-chlorobenzenes (Beurskens et al., 1993). Natural degradative processes play an important role in the recovery of estuarine and marine sediments contaminated with DDT (1,1,1-trichloro-2,2-bis[p-chloro -phenyl]ethane) and DDE (1,1-dichloro-2,2-bis[p-chlorophenyl]ethylene), a toxic degradation product of DDT (Quensen et al., 1998). Microbial degradation of PAHs and aliphatic and aromatic hydrocarbons in marine sediments proceed in the laboratory under aerobic and anaerobic conditions. For certain contaminants, shipboard, short-term mineralization assays have helped provide "lines of evidence" when taken with other site data that show that biodegradation is occurring and is an important process at the site. While these processes may not completely remove contaminants from the sediments, it is possible that microbial populations can degrade contaminants that are loosely bound in the sediments (and thus more bioavailable) or those that partition into porewaters (and are thus otherwise mobile). For this reason, in-place microbial populations may significantly reduce the risk posed by these degradable compounds. For organic halogenated COPCs such as PCBs, dioxins, halogenated phenols, and brominated flame-retardants, anaerobic biotic processes that lead to significant dehalogenation have been documented, and further dehalogenation and ring-opening may occur via aerobic biotic processes. The consequences of such dehalogenation on the fate and effects of the halogenated COPC is not well understood, and this subject warrants further investigation.

While microbial contributions to MNR through transformation and/or mineralization of contaminants may be limited for the reasons previously discussed, and while rates and extents of biodegradation are very COPC and site-specific, these processes should be evaluated as potential factors in recovery. Microbial activities in sediments are largely responsible for the sediment oxidation/reduction potential, local pH, and the precipitation and dissolution of minerals that compose the surfaces of sediments. As such, microbes are important determinants of the bioavailability of the contaminants in sediments. For example, the AVS that may precipitate and sequester metal contaminants as a by-product of microbial sulfate reduction. Microbially mediated iron reduction also produces surface-associated, reduced iron minerals that are important environmental reductants in the reductive transformation of different nitroaromatic (Heijman et al., 1995) and other compounds.

When assessing a site for MNR, it is also important to identify those parameters that will work against the RAOs set for the site. The incompatibility of an ongoing source of contaminant with MNR has already been discussed. Even without an ongoing source, risk assessments may show that the COPC presents an immediate and significant harm to human health and the environment, and that active remedies can achieve RAOs much more rapidly than a MNR solution (Sediment Management Working Group, 1999). Site-specific characteristics that will work against the processes that support MNR include insufficient deposition of clean sediments and/or a high-energy environment in which sediments are constantly resuspended and transported. Sediments with a low surface area or organic content may not sorb the contaminants, leaving them available for diffusion to the water column. Microbial processes may transform contaminants into more soluble and/or bioavailable forms. Microorganisms may dissolve solid phase minerals that can be responsible for precipitating and sequestering the contaminants. Methylation of inorganic mercury in surficial sediments to produce the more toxic and bioaccumulative methylmercury is an example of a microbial process acting against MNR goals. In addition to these undesirable site-specific processes, a drawback to natural recovery that does not depend on degradation is the fact that the contaminants stay in place. Therefore, MNR as a remedial option may be most effective in

systems that show little bottom scour and high sedimentation rates. Nevertheless, MNR is potentially a favorable remedial measure when the site-specific ecological risk is low, the habitat is mostly healthy, and other site conditions are favorable.

Sites exhibiting natural processes ineffective for or antagonistic to controlling the mobility and availability of the COPC are not necessarily contraindicated for MNR as a remedial strategy. Engineered remedial solutions such as active capping methods or limited removal of contaminated materials can be designed to overcome undesirable site-specific characteristics while taking advantage of the processes already acting at the site in support of MNR.

Many current sediment management documents are built on an assumption that has major potential impacts on how sediments will be managed in the future. This assumption results in part from extrapolation of findings from a report that focused on the management of PCB-contaminated sediments (NRC, 2001), but which has frequently been cited as a document on the management of contaminated sediments in general. PCBs are largely anthropogenic, recalcitrant (though we are learning a bit about their biotransformation in some environments) and have a strong tendency to bioaccumulate and biomagnify. Thus, PCBs and some other contaminants are defined as persistent bioaccumulative toxins (PBTs). These characteristics have serious implications for management strategies—their presence in sediments, even at relatively low concentrations, may present a continuing risk up the food chain and, thus, issues such as dispersion, mixing, bioturbation, etc., can present risks for remedy failure. However, note that for many contaminants, almost every potential path for exposure (diffusion, advection, mixing dispersion, etc.) also presents a potential for recovery of the sediment (see, for example, Reible and Thibideaux, 1999). What risk assessors and managers must determine is whether the relative rates of recovery and exposure are balanced out in a protective way—can advection slowly “clean” the sediments without generating toxic fluids for biota? Can mixing dilute sediments to a non-toxic level? Does bioturbation aid in this process? In some cases, these processes may be beneficial. What processes are critical to determine the projected mode and/or mechanism of toxicity that are of concern? Do transport processes increase or decrease these risks? For PBTs, because of their properties, these pathways may pose serious risks. However, many contaminants in sediments (most metals, some PAHs) are toxic primarily because of their high concentrations in the sediments. Non-toxic, often, even natural levels of these chemicals, are in sediments. In these cases, if carefully evaluated, dispersion, mixing, and other mechanisms *may* be useful routes to recovery, and dispersal with dilution may in some cases be a desirable process. Risk assessors and managers should base their CSMs on mode of risk (acute, chronic, bioaccumulation, etc.), contaminant of concern, and type of sediment environment. Design of a CSM should identify the pathways and mechanisms of exposure of concern. Then, the relative risks and benefits of disturbances for a site can be evaluated and considered in an evaluation of MNR.

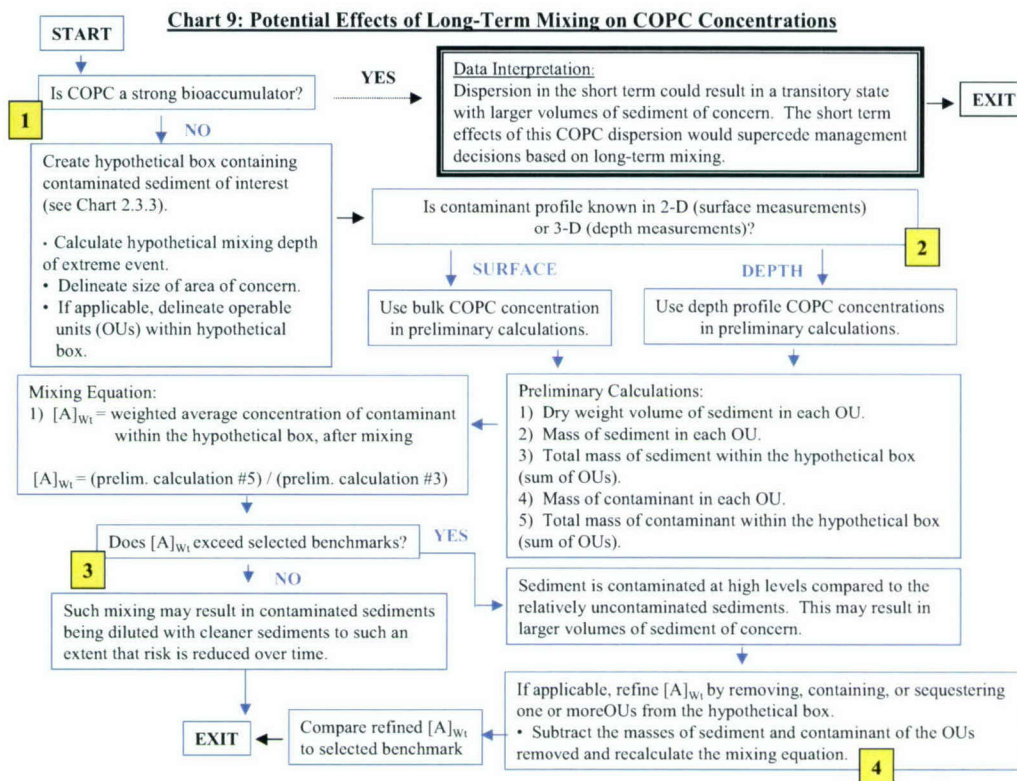
If the main risk drivers are not PBTs, then the potential risks and benefits of various mixing scenarios can be evaluated. “End-member” mixing scenarios can be used to evaluate the potential increases or reductions in risk posed by sediment mixing (caused by either natural or anthropogenic long-term or extreme events) with and without the containment or removal of selected OUs. These calculations aid in the selection and evaluation of management options for further investigation. While it is generally improbable that whole volumes of sediment will be mixed, end-member calculations allow evaluation of worst-case scenarios, and identify the use, necessity, or futility of further, more detailed modeling and investigation. [SOP 2](#) outlines the numerical approach to these evaluations. **Case Study 9** provides many scenarios in which the impacts and benefits of various mixing scenarios are

investigated. As [Chart 9 \(Appendix B\)](#) shows, surface and depth concentration data can be used to delineate various strata of contaminated sediment and calculate mixing effects (**Figures 15-1 through 15-4**). The various scenarios in this case study show that mixing over time can either result in increased or decreased risk (**Figures 15-5 through 15-8**). At times, if a hot spot is contained or removed, further mixing or dispersion can result in natural recovery. Of course, in a depositional environment, if sources have been controlled, burial and the input of clean sediments will enhance these processes. A detailed model of the potential effects of these processes over time is justified if indicated by the end-member calculations.

Where natural processes are relied on to achieve cleanup objectives, long-term monitoring and performance standards must be developed for the successful application of MNR. It is critical to choose accurate and relevant indicators for an evaluation of permanence at a given site, including data that confirm the presence of MNR mechanisms and quantify rates, trends, and expected permanence.

Unlike MNA for contaminated groundwater, MNR for sediments has no prescribed approach or list of chemicals to measure what would establish the extent of natural recovery through contaminant weathering. To support MNA as a remedial option for contaminated groundwater, three lines of evidence are often required: (1) loss of contaminant mass in the field, (2) contaminant and geochemical analysis (presence and distribution), and (3) microbiological evidence. MNA correlates electron acceptor gradients with contaminant gradients in groundwater to establish ongoing electron acceptor processes such as aerobic respiration or anaerobic respiration under nitrate-, iron-, manganese-, or sulfate-reducing conditions or methanogenesis. In contrast, because of higher natural organic material content of sediments, contaminants are primarily sorbed to sediment solids, so they do not generally create contaminant plumes that affect electron acceptor gradients. Oxidizing conditions in sediments generally exist only at the top few centimeters or even millimeters of surface sediments, providing a very limited zone where oxygen is available for aerobic biotransformation of sediment contaminants. Beneath the aerobic zone, sediments are typically dominated by a single electron acceptor process such as sulfate reduction in marine sediments or methanogenesis in freshwater sediments. However, current advances in observing the benthic interface using time-lapse Sediment Profile Imaging and two-dimensional oxygen optrodes, as well as observations on porewater dynamics in micro-flow environments, make it clear just how dynamic surface sediments are, and seriously undermine the image of a static, buried, anoxic system (see, for example, Solan and Kennedy, 2002). Laboratory results on PAH responses to aeration, combined with Office of Naval Research (ONR)-funded work demonstrating anaerobic capacity, as well as biomarker work and field observations of PAH patterns in disturbed versus quiescent sediments suggest strong evidence that PAH-contaminated sediments will continue to recover long after deposition.

CASE STUDY 9: MIXING SCENARIOS



In this case study, Cu was identified as a metal COPC. Because Cu is not considered a strong bioaccumulator, evaluation of the long-term risks and benefits of mixing continued (box 1 in flowchart above). Both surface and depth contaminant profiles were known and used to delineate the hypothetical box (strata) of interest for mixing (2). The ER-M value of Cu was selected as a benchmark.

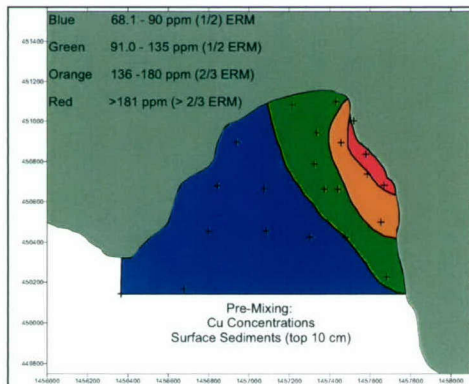


Figure 15-1. Surface Cu concentration profiles.

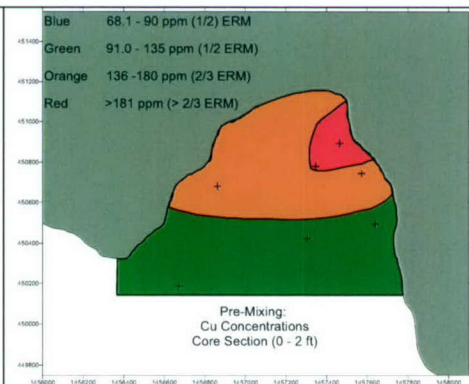
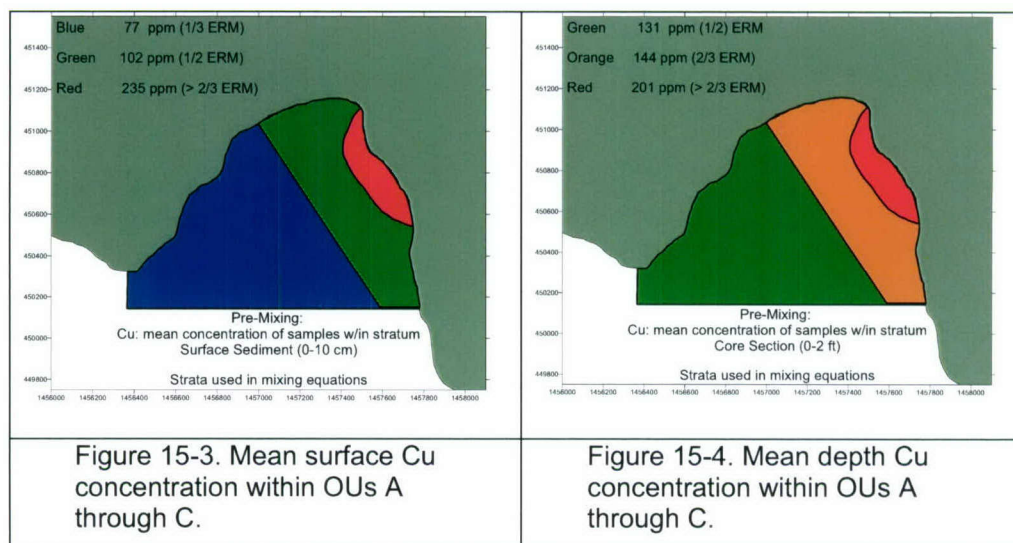
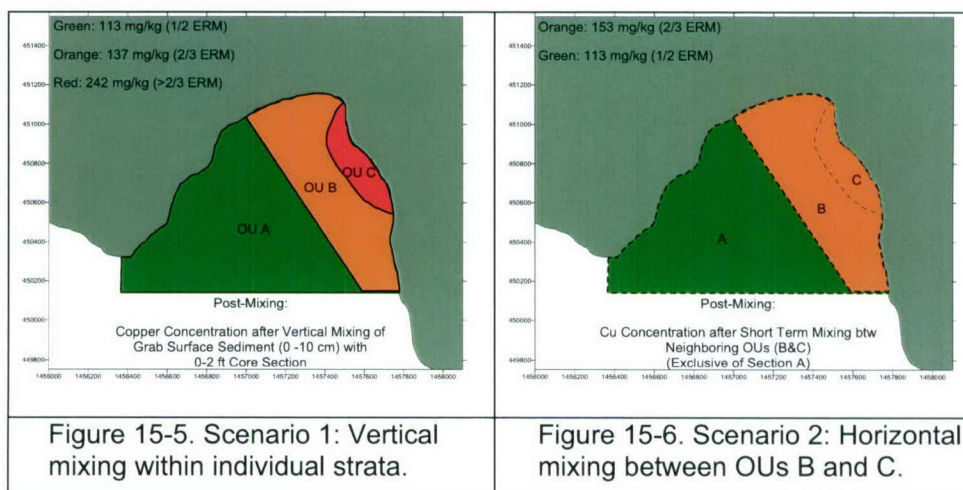


Figure 15-2. Depth Cu concentration profiles.

CASE STUDY 9 (continued)



Various scenarios were formulated for the site based on management objectives and remedial options. The mixing effects of these different scenarios were evaluated using preliminary and mixing equations (See SOP 2, Appendix A) and compared to the selected benchmark (3). The first three scenarios in this case study assessed the risks, benefits, or consequences of leaving sediment in place with no controls. The first scenario examined the effects of localized mixing within each stratum. The vertical mixing of surface and deeper sediments resulted in concentrations less than $\frac{1}{2}$ ER-M in the two larger strata (OUs A and B) and concentrations near ER-M in the smallest stratum (OU C). Another scenario looked at the short-term mixing of sediment between the most contaminated neighbouring OUs (B and C). Such mixing led to a decrease in overall COPC concentration (below the selected benchmark) in the highly contaminated upper right section of the basin (OU C).



CASE STUDY 9 (continued)

This scenario was expanded to investigate the effects of long-term horizontal mixing of the entire basin. Although it is extremely improbable that an entire site would ever be mixed, this scenario provides a worst-case example of the unknown degree of mixing, resuspension, and transport that may occur. In this scenario, mixing resulted in an overall COPC concentration of less than $\frac{1}{2}$ ER-M throughout the basin.

A final scenario was developed to study the effects of removing or containing a section of the site (4). For this scenario, the most contaminated portion of this site (OU C) was capped while the remainder of the basin was mixed. The results were similar to those of the previous scenario (overall COPC concentration less than $\frac{1}{2}$ ER-M).

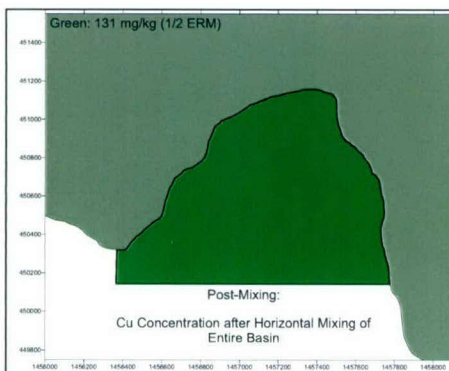


Figure 15-7. Scenario 3: Horizontal mixing of the entire site.

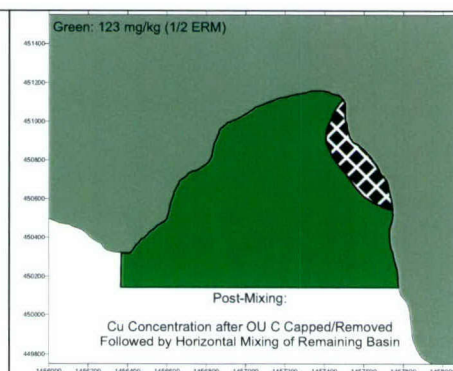


Figure 15-8. Scenario 4: Horizontal mixing after containing sediment within OU C.

Bacterially mediated biodegradation within sediments is expected to be an important process for many aliphatic, aromatic, and chlorinated hydrocarbon compounds. Recently, understanding of these processes in marine systems has increased significantly (Coates et al., 1996; Coates et al., 1997; and Dyksterhouse et al., 1995). However, because inorganic contaminants do not biodegrade, little is known about the biodegradation potential of many complex organic compounds, and many other organic compounds resist biodegradation or degrade only under specific conditions. It is critical to determine what portion of the cumulative COPC hazard can be attributed to potentially degradable compounds before biodegradation is considered in too much detail. Clearly, even if very degradable compounds exist in sediment, biodegradation does not merit much attention if they comprise a small fraction of the total risk because even a complete biodegradation would not lead to a significantly lower risk. One useful tool for such an assessment is the Hazard Quotient (HQ). In the following case study (**Case Study 10**), a significant proportion (30 to 40%) of the total PAH is attributable to the LMWPAHs (Figure 16-1). Hazard quotients, as a function of COPC, are calculated, and plotted in Figure 16-2. For OUs 2 and 3, the contribution of PAHs put the HQ over an acceptable level, while for OU 1, other, less or non-degradable COPCs cause the threshold exceedance. To determine whether successful biodegradation alone is enough to reduce risk at the site, HQs are then re-calculated with the end-member assumption that 80% of the LMWPAHs and 30% of the HMWPAHs will biodegrade (Figure 16-3). While HQs are reduced in all OUs for OU 3, risk is reduced to acceptable levels, but for OU 2, it still leaves a considerable risk, even from PAHs. For OU 1, the risk from other COPCs remains unacceptable (Figure 16-4). Such an evaluation does not prove that biodegradation will provide sufficient natural attenuation at a site. Proof requires much more extensive evaluation, as discussed below. However, this evaluation of site data provides an indication of which sites justify further investigation for biodegradation (in this case, just PAHs, though other classes of contaminants can be handled the same way). The literature is rife with detailed investigations of PAH biodegradation at sites where they are not the primary risk or decision driver, and where even complete biodegradation will lead to a trivial reduction of net risk. While these studies are fascinating at a scientific level, justification for them from a site-specific risk management viewpoint is small. A simple evaluation of COPC mix at a site will help properly allocate site investigation resources.

Due to the inherent complexity of natural estuarine sediment systems, it is virtually impossible to "prove" to what extent biodegradation can be expected to reduce contaminants. Instead, one can draw conclusions from many lines of microbial and biogeochemical evidence (see Table 4); an assessment of the role of biodegradation can incorporate the following main lines of evidence based on samples collected from cores, grabs, mini-profilers, porewater samplers, seepage meters, and/or surface water:

1. Examination of changes in contaminant fingerprints over time or space, indicative of biological, as opposed to physical, processes. In this approach, ratios or trends between components that have very similar physical behavior but differ in their amenability to biodegradation are compared to distinguish biodegradation from abiogenic processes such as physical weathering, volatilization, and leaching (Blumer, Ehrhardt, and Jones, 1973; Kennicutt, 1988; Pritchard et al., 1992; Page et al., 1995; Apitz and Meyers-Schulte, 1996). In such an approach, changes in contaminant fingerprints from the source into and through the contaminated region can provide insight into whether and how further microbial processes should be examined. While this insight can indicate microbial processes, it can be difficult to unequivocally separate signature changes due to biodegradation from signatures

due to weathering, mixing, or differential sources. Taken with other lines of evidence, however, fingerprint evidence can be fairly compelling.

2. Examination of microbial “capacity” based on general measures of bacterial production that serve as indicators of the biodegradation process, combined with compound-specific assays for labeled hydrocarbon mineralization rates. In such analyses, samples are taken from the field and immediately tested for their ability to metabolize labeled and spiked carbon and target contaminants, under as near as possible to in situ conditions (e.g., Montgomery et al., 1999). With this line of evidence, one can demonstrate whether or not microbes that can perform intrinsic biodegradation are in samples. Because such measures can be made rapidly, and with very low spike concentrations, they are less subject to post-sampling population changes than are laboratory slurry studies. If this is so, these assays may not predict rates and extents for sediment “recovery” in the sense of return to background values. However, the observation that in-place microbial populations can rapidly degrade an added spike (rather than require a long time for adaptation) strongly suggests that some degradation of the compound of interest (or a closely related compound) is going on in situ. Regardless of how low COPC levels will or will not get in sediments, such activity is important for risk reduction because it should eliminate loosely bound, dissolved, and bioavailable PAHs. Currently, such assays are conducted with a limited set of compounds.

3. Laboratory slurry and flask biodegradation studies. In these assays, sediments are placed in vials, flasks, reactors, micro- or mesocosms, kept aerobic or anaerobic (depending on the question being asked). Generally, abiotic control samples are poisoned or killed in some other way. Sediments are subsampled over time, extracted, and analyzed for target compounds and microbial populations. Degradation is inferred from a decrease in extractable target compounds over time (relative to abiotic controls) and evidence of microbial growth. These experiments have the advantage that an unlimited number of compounds (such as a broad suite of PAHs) can be tracked at once. If well designed, they may give an indication of how much of a compound is easily degradable. However, they are subject to many problems. First, because these studies are conducted for hours to months, one can argue that they are not representative of in-situ conditions—populations can adapt and shift in response to experimental conditions. They are subject to a many flask effects—nutrients can be depleted, pH can drop, toxic by-products can build up. Assays based on changes in extractable materials are also sensitive to various factors that can affect extractability, such as pH, ionic strength, etc. Because they are slow and labor-intensive, the number of replicates that can be carried out is limited, which clouds variability. However, because many compounds can be tracked at once, these assays provide an important line of evidence if carefully designed and interpreted.

CASE STUDY 10: MONITORED NATURAL RECOVERY

Potential Effects of Monitored Natural Recovery (PAHs)

MNR of sediments as a remedial option relies on natural environmental processes to permanently reduce risk and requires careful assessment, modeling, and monitoring. Principal natural processes include deposition/burial, dispersion, mixing irreversible adsorption, and chemical and biological reactions. Bacterially mediated biodegradation within sediments is expected to be an important process for many aliphatic, aromatic, and chlorinated hydrocarbon compounds (e.g., PAHs). In cases where degradable compounds represent a significant portion of the risk, then biodegradation should be considered. Hazard Quotients can be useful for determining relative risk of individual COPCs to the total suite of risk-drivers. The following example illustrates such a case. At this site, PAHs, Cd, and Hg were the principal contaminants of concern. As discussed in Case Study 7, LMWPAHs are more biodegradable than HMWPAHs. At this site, a significant proportion (30 to 40%) of the total PAH is attributable to the LMWPAHs (Figure 16-1).

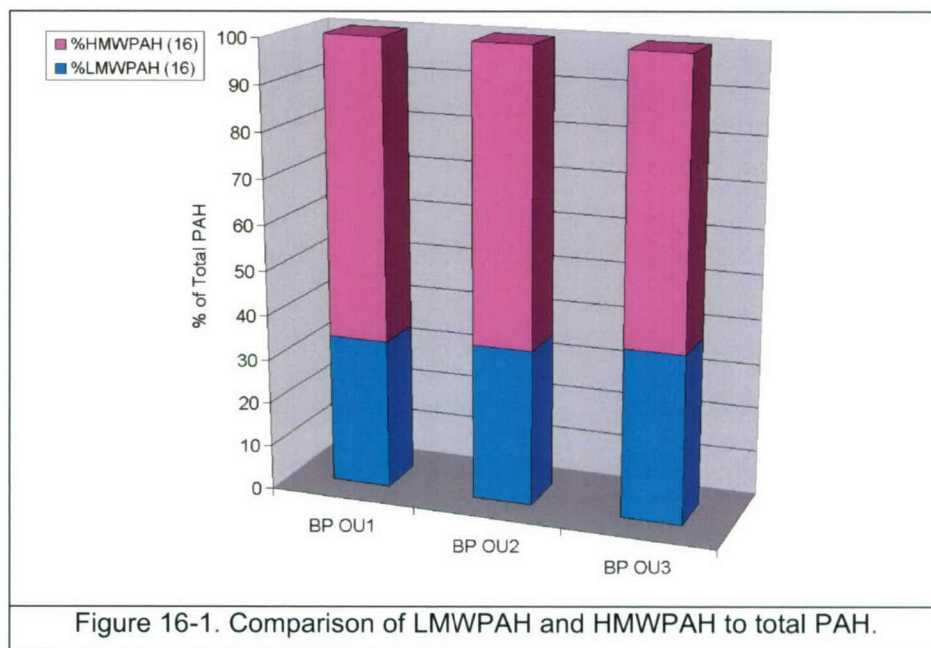


Figure 16-1. Comparison of LMWPAH and HMWPAH to total PAH.

Hazard Quotients, as a function of COPC, were calculated and plotted (Figure 16.2) using the following assumptions (Figure 16-3). For OU 1, the non-degradable COPCS (Cd, Hg) put the HQ(sum) over an acceptable level, while for OUs 2 and 3, the contribution of the PAHs cause the exceedance. Based on a MaxHQ Limit of 4.00 (HQ = 1.00 for four COPCs), then OUs 1 through 3 present risk before MNR. Only OU 3 does not present a risk after MNR (Figure 16-4).

CASE STUDY 10 (continued)

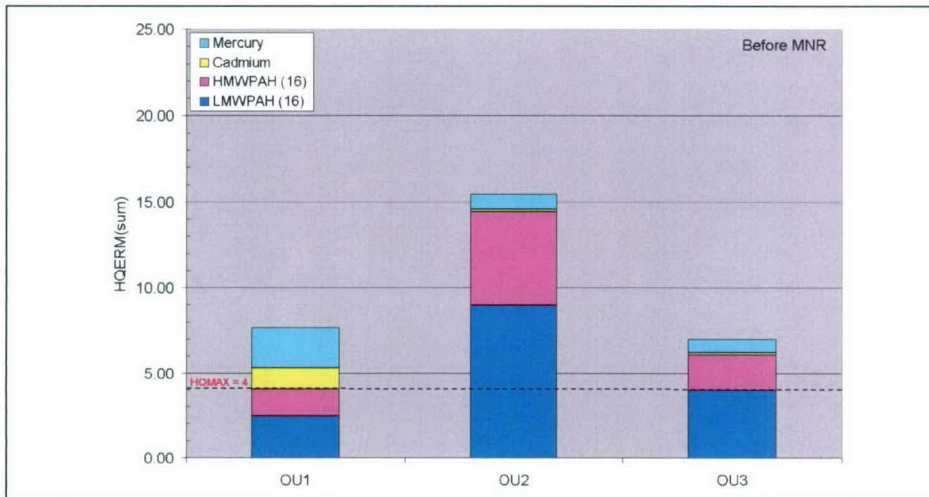


Figure 16-2. HQs as a function of COPC (calculated and plotted).

PAH Scenario Assumptions:

- ☐ HQPAH: use ERM
- ☐ HQMetals: use ERM
- ☐ HQ>1: unacceptable risk
- ☐ HQ<1: acceptable risk
- ☐ Max HQ: 4.00
- ☐ Before: no MNR

After: MNR for PAHs assuming 80% reduction in LMWPAH and 30% reduction in HMWPAH. No change in metal concentrations.

Figure 16-3. PAH scenario assumptions for MNR determinations.

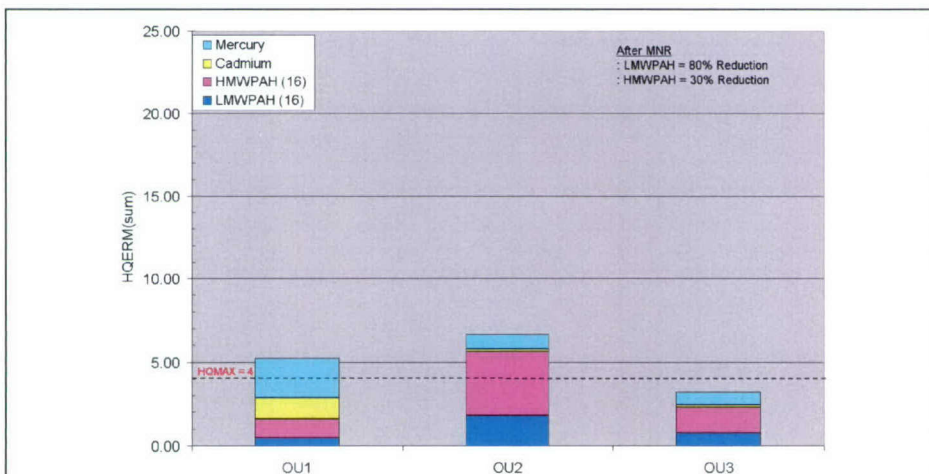


Figure 16-4. Recalculation of HQs using PAH biodegradation rates.

4. Examination of metabolic by-products of biodegradation. In many cases, contaminant fingerprints will show the appearance of compounds that are indicative of microbial activity such as degradation intermediates. While this work is in its early phases (e.g., Elshahed et al., 2001), such processes are well established in groundwater systems. A growing body of literature is being published on such metabolites and, thus, a current literature search should be performed before considering such an effort.

5. Examination of microbial populations (taxonomy). As research into biodegradation in sediments progresses, much is being learned about the identity of specific contaminant degraders, and assays for their presence are under development. However, though much has been learned about what microbial species are present in laboratory samples, this process can be a very complex process, especially in marine systems, and much remains to be learned about consortia effects, etc. While the presence of known degrading populations is a strong positive indicator for the potential for natural attenuation, the absence of such known populations does not indicate that degradation will not occur—many populations must still be identified, and assays are limited.

Tables 3 through 5 show various field measurement and analytical tools that may be used to evaluate the effectiveness of MNR in sediments. Table 3 shows physical transport measurement tools. Table 4 shows tools to evaluate the magnitude and extent of contaminant weathering (including biotransformation/biodegradation) studies. Table 5 shows tools to evaluate ecosystem impacts due to contaminated sediments and ecosystem recovery studies that may be conducted.

The tools identified in Tables 3 and 4 focus on sedimentation and weathering because these are often the two principal mechanisms contributing to the natural recovery of sediments. Sedimentation (Table 3) acts to provide a clean layer and protect the benthos, water column, and resident fish from contaminant exposure. Weathering serves to stabilize contaminants and can provide permanent reductions in contaminant bioavailability and toxicity. Weathering processes (Table 4) include physical (adsorption, sequestration, dilution, and volatilization), chemical (sequestration, hydrolysis, photolysis), and biological (biodegradation/biotransformation) mechanisms, and can be measured by comparing weathered sediments with less weathered sediments or known contaminant profiles from the literature. For example, existing PCB histograms are commonly compared to known histograms of Aroclors reported in the literature if the Aroclor source is known.

Table 5 focuses on ecological measurements that can be used to assess the health or recovery of the sediment and surrounding ecosystem. As discussed above, MNR is by definition a risk management strategy. Thus, an assessment of the efficacy of MNR necessitates an assessment of risks that sediment contaminants pose on the ecosystem and ecosystem recovery or potential for recovery. For monitoring to provide insight into remedy efficacy, it is critical that baseline values be established. In natural systems, measurable indicators of environmental health can vary significantly as a function of space, time, season, etc. Without solid information about the variability of these parameters, and without careful and consistent sampling and analyses to minimize controllable sources of variation, demonstrating changes over time will be difficult. A discussion on the monitoring of remedial effectiveness is available at <http://www.sediments.org/sedmgmt.pdf>.

Modeling of some sort is always needed in the assessment of MNR, that is, a careful understanding of sedimentation rates, contaminant sources, sediment transport, benthic mixing, and bioaccumulation of sediments is required to understand and effectively

implement MNR. The most effective sediment models are those that have a strong basis in physics, chemistry, and biology, and contain a minimum number of adjustable parameters. Models strive to match/explain past history and to accurately predict future performance. For MNR, they should match any recovery that has already occurred. To suggest that MNR is a viable alternative, the model should also predict that recovery will continue to occur, or that it will at least be adequate and sustainable. Modeling is used in the assessment of MNR in at least two site situations: (1) where effects have been observed (e.g., fish concentrations) and where one wishes to evaluate whether the sediments are the cause, or that the effects will diminish with time; and (2) effects have not been observed, although sediment concentrations have been observed and one wishes to evaluate whether effects will result in the future. In both instances, recovery processes, permanence, and stability are key issues.

Table 3. Field measurement and analytical tools for evaluation of sedimentation and in situ burial of contaminated sediments.

Process	Measurement	Tools
Sedimentation under differing hydraulic loading conditions	Establish the natural sedimentation, resuspension, and scouring rates	<ul style="list-style-type: none"> • Measure in situ sediment depths over time (e.g., bathymetric surveys) • Evaluate historical sedimentation using ^{210}Pb, ^{137}Cs, or similar dating of sediment cores • Develop a hydraulic sedimentation model to characterize sedimentation
Sedimentation under high flow conditions (turbulent mixing)	Examine the effect of surface sediment mixing with clean sediment, and examine sediment resuspension, particularly during high flow periods	<ul style="list-style-type: none"> • Examine the water velocity distribution under differing flow conditions • Measure sedimentation and sediment scouring processes under differing flow conditions (bathymetric surveys, sediment traps)
Sedimentation under storm conditions	Examine the effect of surface sediment mixing, sediment scouring, and sediment transport and deposition under storm events	<ul style="list-style-type: none"> • Conduct storm event sediment and water column sampling (grab samples, sediment traps) • Measure sedimentation and sediment scouring processes under differing flow conditions (bathymetric surveys, sediment traps) • Measure critical shear stress with in situ or laboratory flumes
Vertical diffusive flux	Determine the depth at which sediments need to be buried by natural sedimentation to protect the water column, surface biota, and fish	<ul style="list-style-type: none"> • Measure the diffusive flux for surface sediments using laboratory column studies • Measure the diffusive flux for exposed and buried sediments using in situ benthic flux chambers
Vertical advective flux	Determine the advective contaminant flux, and depth at which clean sediments need to bury contaminated sediments to protect the water column, sediment biota, and fish	<ul style="list-style-type: none"> • Measure the advective flux for exposed and buried sediments using laboratory column studies • Measure the vertical advection of contaminants in situ using seepage flux meters
Vertical groundwater advection	Determine whether there are groundwater advective zones	<ul style="list-style-type: none"> • Perform hydraulic studies: Dye studies Piezometer studies Seepage flux meters Multilevel pressure transducers Radon isotope studies
Sediment mixing through bioturbation	Evaluate the extent of sediment mixing and contaminant transport through bioturbation	<ul style="list-style-type: none"> • Sediment age dating analyses (e.g., ^{210}Pb) may be used to assess bioturbation • Assess macroorganisms and their reported mixing depths • Underwater photography can be used to assess surface benthic activity • Sediment profile imaging can show depth and distribution of benthic activity

Table 4. Field measurement and analytical tools for the evaluation of in situ contaminant weathering, including biotransformation/biodegradation.

Process	Measurement	Tools
Contaminant weathering using forensic analyses	Examine the magnitude and extent of contaminant weathering that has occurred in the sediments for historically deposited contaminants	<ul style="list-style-type: none"> • Conduct contaminant fingerprinting at various sediment depths to establish a historical contaminant profile • Use conservative tracers (e.g., hopane for petroleum hydrocarbons) or other biomarker to assess the magnitude and extent of contaminant weathering • Examine organic/inorganic geochemical indicators (e.g., redox, dissolved oxygen, total organic carbon, etc.) • Conduct laboratory weathering experiments
Anaerobic biotransformation	Determine whether anaerobic biotransformation occurs under natural conditions and establish biotransformation rates	<ul style="list-style-type: none"> • Establish the occurrence of anaerobic biotransformation in laboratory by comparing contaminant losses in live and killed sediments and/or by conducting ¹⁴C-contaminant studies • Conduct long-term microcosm studies using aged contaminated sediments to develop contaminant biotransformation rates • Examine contaminant distribution shifts (e.g., accumulation of higher-molecular weight PAH or lower chlorinated PCB) that may reflect contaminant biotransformation (it may not be possible to distinguish biotransformation from other weathering phenomena) • Use biomarkers (e.g., genetic and degradation intermediates) to positively identify biological activity
Aerobic biotransformation	Determine whether aerobic biotransformation occurs under natural conditions and establish biodegradation rates	<ul style="list-style-type: none"> • Establish the occurrence of aerobic biodegradation in laboratory microcosms by comparing contaminant losses in live and killed controls and/or by conducting ¹⁴C-contaminant studies • Conduct long-term microcosm studies using aged contaminated sediments to develop contaminant biodegradation rates • Examine contaminant distribution shifts (e.g., accumulation of higher-molecular weight PAH or lower chlorinated PCB) that may reflect contaminant biotransformation (it may not be possible to distinguish biotransformation from other weathering phenomena) • Use biomarkers (e.g., genetic and degradation intermediates) to positively identify biological activity
Bioavailability	Assess availability of contaminants at low concentrations to microorganisms, to establish a low-concentration threshold where biotransformation does not occur.	<ul style="list-style-type: none"> • Conduct microcosm studies using unamended sediments with a range of initial contaminant concentrations, from < 30 ppm to the maximum observed concentration • Compare sediment contaminant concentrations to literature-reported bioavailability limits
Contaminant partitioning	Assess contaminant sorption in sediments, and compare to literature sorption values	<ul style="list-style-type: none"> • Conduct batch contaminant laboratory sorption studies using sediments and water from the site • Use literature values for sorption coefficients

Table 5. Field measurement and analytical tools for evaluation of ecological recovery by natural attenuation.

Process	Measurement	Tools
Water column recovery	Monitor changes to the water column before and after source control measures are implemented. Determine if low-level contamination persists in the water column, in the absence of measurable contaminant concentrations.	<ul style="list-style-type: none"> • Monitor sediment, water column, and air (e.g., atmospheric) contaminant concentrations along contaminated portions of the site to assess sediment and water column recoveries • Use caged fish, caged mussels, trapped fish to measure contaminant bioaccumulation from exposure to the water column • Use resin traps to measure the potential for bioaccumulation from exposure to the water column
Fish and biota recovery	Examine how quickly fish and sediment biota respond to source control measures and sediment remedial actions	<ul style="list-style-type: none"> • Conduct fish and sediment biota sampling over time to assess in contaminant concentration reductions in plant and fish tissue • Conduct population assessments to examine population changes due to sediment contamination and recovery • Conduct bioassays to assess the health of sediments or water and potential toxic impacts of contaminants on resident biota
Bioaccumulation studies	Establish primary bioaccumulation pathways from sediment biota to fish and/or mammals; determine whether deep or shallow sediment biota (or both) contributes to fish contamination	<ul style="list-style-type: none"> • Conduct sediment biota and fish surveys and develop an ecological or human health contaminant exposure model • Use caged fish, caged mussels, trapped fish to measure the potential for contaminant bioaccumulation

At a minimum, a reliable CSM is needed. This conceptual model should consist of a qualitative or quantitative statement and a diagram of how the various physical, chemical, and biological processes affect the overall risk at the site. Under certain circumstances, in a reliably low-energy environment with no ongoing sources and no measurable effects in the water column or biota, a qualitative conceptual model might suffice for the selection of an MNR remedy. For a more complex site, a more detailed mathematical model is usually necessary. A discussion of CSMs is available at <http://www.sediments.org/sedmgmt.pdf>.

Mathematical models for sediments have been developed independently in groups that build sequentially on one another. One group, the hydraulic models, forms the main foundation in describing the flows and associated stresses, primarily for riparian systems. They are generally open-channel models, which include as their inputs the size and shape of the streambed or water body and the range of flows expected from various sources. Sediment transport models, built on the previously described hydraulic models, are well developed for non-cohesive sediments (i.e., sands) but less reliable for cohesive forms (i.e., muds). Next in sequence are the models for physical and chemical transport and transformation of contaminants that are linked to the hydraulic and sediment transport models. All models must be site-specific and contaminant-specific in their application, particularly when progressing beyond hydraulic and sediment transport models. Beyond physical and chemical transport models are those models that describe the biological processes, including food chains. In using sediment modeling tools, the outputs from the more basic model groups provide the inputs to the next group, and so on. Normally, the mass transport and biological processes are not expected to feed back to the more basic processes such as hydraulics, but one must always be alert to

site-specific exceptions, for example, the effects of bioturbation on the mass transfer of contaminants.

Models are “calibrated” using measured data to set the values of any adjustable parameters. A strong basis in science and a minimum number of parameters gives the model credibility in predicting the future performance. Data-gathering tools and techniques discussed elsewhere in this section are used to develop the data required for model calibration. Once calibrated, an important function of a model is to predict the rate at which recovery will occur. MNR is often assessed relative to the time frame in which overall risk is reduced, relative to other remedial approaches—particularly relative to removal of the contaminated sediments. To assess MNR against other alternatives, the same model should be applied, as much as practical, to each alternative. For consistency, the same model might be asked to predict not only the recovery scenario for MNR by itself, but also the recovery rate by natural processes following a removal action.

With all their strengths, a fundamental rule that always applies to models is that models and other predictive tools should never take precedence over something that can be measured directly. For example, models and other surrogates should not be used to predict current levels of contaminants in fish tissue if fish can be caught and measured directly. The true usefulness of models is to predict future states that cannot be measured directly, or to guide sampling and data collection. Measurement tools are used to characterize the present state.

Ideally, MNR should not be assessed by itself, but in comparison to other remedial approaches. Combining assessment steps or data gathering for multiple remedies into a minimum number of field investigations is economical, and the complexity of most sites does not render them amenable to single, ideal solutions. Many sites must be addressed using multiple remedial approaches. Natural recovery will always play a key role as the main approach (with extensive monitoring) or as a means of attenuating residues or dispersed materials left after a remedial action. Other remedies that should be assessed along with MNR include removal, capping, assisted natural recovery, hydraulic modification, and all combinations. The overall assessment question should not be whether MNR achieves some idealized state where all contaminants are destroyed or otherwise inactivated. Instead, the fundamental question is whether MNR can achieve protective levels in a time comparable to other remedial approaches or in a way that is less damaging to health and the environment than other remedial alternatives.

More discussion of MNR can be found in “Implementation Guide for Assessing and Managing Contaminated Sediment at Navy Facilities” (Naval Facilities Engineering Command, 2003). This document is available at http://enviro.nfesc.navy.mil/erb/erb_a/restoration/fcs_area/con_sed/ug-2053/ug-2053-sed.pdf

4.4 IN SITU CONTAINMENT (ISC)

If risks are too high or recovery rates are too slow for MNR, but risks and COPC mobility are not considered excessively high, contaminant mobility and bioavailability can be reduced by some form of in situ containment (ISC). **Case Study 9 (Section 4.3)** illustrated the evaluation of the effects of ISC (or removal) of selected units on the long-term risks and benefits of mixing. While many models exist, few field studies discuss the long-term efficacy of ISC on contaminated sediments. A significant body of literature on capping and containment is available at <http://www.wes.army.mil/el/dots/doer/pdf/trdoer1.pdf>. Containment will be most successful if contaminants are primarily bound to sediments, rather than dissolved in

porewaters. Because some forms of ISC can be seen as an accelerated form of sedimentation, many tests in Table 3 for the evaluation of MNR feasibility are also applicable to ISC. Essentially, in situ containment adds transport retardation terms to an evaluation of recovery, where capping (barrier) material is added. Stability, with and without the cap, should be evaluated, as well as fluid transport. Caps are generally considered inappropriate if advection, instead of diffusion, drives dissolved contaminant transport. However, a growing body of research into active caps shows that the caps may bind dissolved contaminants as they pass through the cap or enhance biotic or abiotic degradation processes. Thus, ISC may be appropriate for sediments in more advective environments in the future.

More discussion on in situ capping can be found in "Implementation Guide for Assessing and Managing Contaminated Sediment at Navy Facilities" (Naval Facilities Engineering Command, 2003).

Monitoring must be conducted before, during, and after construction of the cap to ensure that the cap was correctly constructed and is effectively isolating the contaminants. The integrity of the cap must also be verified. Guidance on designing and implementing a monitoring program for a capping project is in the USACE Waterways Experiment Station (WES) Technical Note DRP-5-07 (June 1992; <http://www.hsrb.org/capping/monitor-note.html>).

Additional detailed information on in situ capping can be found in the following places:

- The U.S Navy has an in situ capping technology Web page: http://erb.nfesc.navy.mil/restoration/technologies/remed/contain_remove/cr-04.asp.
- The U.S. EPA-sponsored Web site: <http://www.hsrb.org/capping/>
- U.S. EPA's Assessment and Remediation of Contaminated Sediment (ARCS) Program, *Guidance for In Situ Subaqueous Capping of Contaminated Sediments* (Palermo et al., 1998; <http://www.epa.gov/glnpo/sediment/iscmain/>)

4.5 IN SITU TREATMENT (IST)

In situ treatment (IST) can be divided into two broad categories: (1) in situ stabilization, which decreases the mobilization potential of contaminants because they have been "fixed" in place by biological or chemical means, and (2) in-situ treatment that accelerates processes that degrade contaminants, i.e., reduce the toxicity of contamination within the sediments. As with MNR, it is assumed that sediments are sufficiently stable so that in situ processes can be conducted without excessive risk.

A growing body of evidence suggests that sediment removal can sometimes result in more ecological damage, or after great expense, not show measurable ecological improvement (e.g., Thibideaux et al., 1999). Because of volumes and costs involved, some sediment sites will be managed in place. While sediment guidance recommends an evaluation of site-specific risks and benefits of management strategies in the feasibility study process, technology-specific and site-specific data on risks or impacts of sediment remedial or management strategies (especially in-place strategies) are sparse. This situation forces site owners to rely on simplistic technology matrices and generic models with minimal site-specific relevance. As a result, when a risk management team chooses to implement passive, in-place or innovative management strategies at a site, convincing a skeptical regulatory community and public can be a daunting task. Many in-place management approaches and technologies are being developed and marketed, but few have been thoroughly evaluated in terms of the effects of the technologies on the bioavailability, toxicity, fate, and mobility of

target and non-target contaminants; data on what characteristics make a site suitable for these approaches do not exist. This lack of data is a barrier to regulatory acceptance and to site owners taking the risk of what are perceived as relatively unproven strategies.

In-place management or containment strategies and in situ remediation technologies must be validated. A toolbox of analytical and modeling tools that support the feasibility process for such in-place management, containment, and remediation strategies must also be validated. Without such data, it is improbable that a wary regulator and stakeholder community will embrace in-place treatment and/or containment processes. However, the research and development community can rarely afford the multi-million dollar efforts necessary to do broad-based, multivariate studies or to meaningfully test sediment remedial strategies in the field. To remedy this problem, one question that should be asked is: Who should bear the cost of such studies if the benefit is for future, not current, applications, but the risk is to the current project? Those who can afford these strategies, primarily vendors and site owners, do not have the incentive to collect the validation data necessary for PRPs and site owners to "sell" these technologies at other sites. Clearly, site owners are at risk if they look deeper into the impacts of their selected remedy than is required by regulators. Technology developers often expect others to pay for validation data. Unfortunately, contractors, regulators, stakeholders, or RPMs have little incentive to streamline the process because the potential risks of innovation are not offset by rewards. If innovative in-place remedial strategies are to be accepted, efforts must be made to balance the risks and benefits with collaborative consortia that bring extra assessment to site demonstrations, but with some regulatory buy-in. The EPA Superfund Innovative Technology Evaluation (SITE) program and the ARCS programs have filled this function well, primarily for soil and freshwater sites, but more sediment-focused efforts are needed.

4.6 REMOVAL VIA DREDGING OR EXCAVATION (FOLLOWED BY EX SITU TREATMENT, DISPOSAL, AND/OR REUSE)

If risks are too high for MNR, and in situ containment and/or treatment are infeasible, removal is the next option. Some see removal via dredging as the only acceptable approach for highly contaminated sediments because it removes sediments (and associated contaminants) from the system, thus permanently eliminating their risk. However, a number of issues remain of concern. First, while dredging does remove contaminants from the marine environment, these contaminants are in most cases (barring treatments resulting in complete contaminant destruction) simply moved to other environments. Potential risks of contaminants in landfills, CDFs, and during transport, as well as risks of dredging to humans and the environment must be considered in a holistic risk assessment. A growing body of literature suggests that in some cases, dredging may lead to increased contaminant risk because it may undermine ongoing MNR processes that exposed previously sequestered contaminants. While little is known about whether such observations represent short-term increases in risk in support of long-term decreases, or a long-term problem, these issues must be considered.

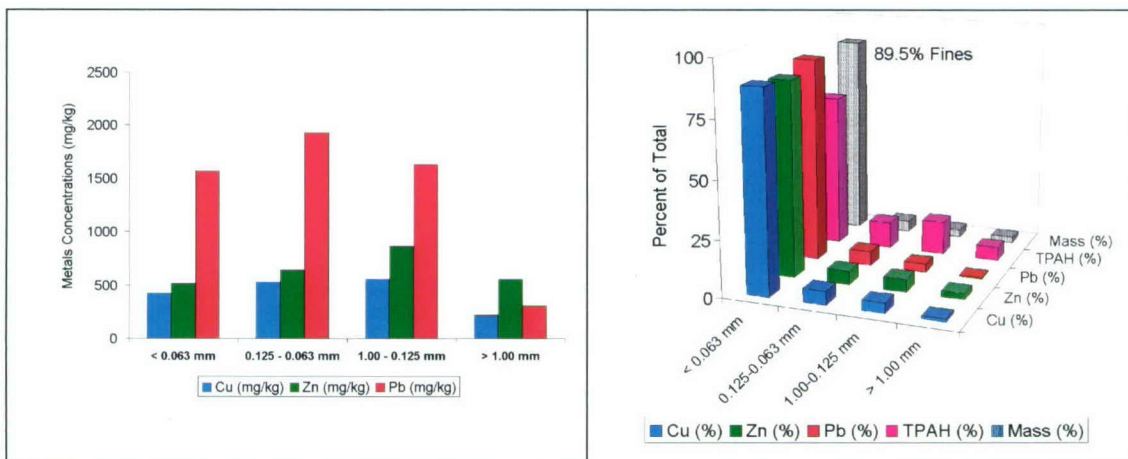
Particularly for dredging, sediment/contaminant data should be considered in two forms. If removal is considered, it is absolutely critical that contaminant distribution data should be available in three dimensions. Thus, composites and grabs do not provide enough information to plan an effective dredging operation because subsurface distributions are not delineated. Particularly in regions where COPC sources have been controlled, unless three-dimensional contaminant distribution information of reasonable resolution is available, the risk that

dredging will lead to the exposure of sediments with higher contaminant loads than those currently at the surface is significant.

On the other hand, when decisions are to be made on treatment or disposal options for the sediments that have been or are to be removed, evaluating sediments with averaged or composited compositions is more logical because sediments may be mixed and combined in transport and treatment. This evaluation can be done through the analysis of composited samples or by conducting weighted averages of three-dimensional analyses of OU sediments (see SOP 1, Appendix A).

One important point to consider when considering dredging is whether dredging will result in dispersion of contaminants. Extensive information on the evaluation of dredging impacts is available at www.wes.army.mil/el/dots or www.wes.army.mil/el/dots/doer. However,

Example 7 illustrates an application of sediment/contaminant distribution data to this question. In this case, evaluation of contaminant distribution and concentration as a function of grain size indicates that very high lead levels are associated with fine-grained sediments. Because fine-grained sediments can be the most mobile when resuspended, this situation should be considered in an evaluation of the potential risks of dredging. However, if these sediments are at the surface and sediments are left in place, dispersion is a risk, and these risks should be balanced.



Example 7. Contaminants are predominantly associated with the fines fraction (< 0.063 mm) in this sediment. Fines are the major proportion of the mass. The high concentrations of contaminants, particularly Pb in the fines, signals potential problems during dredging—controls should be considered.

For a summary of the advantages, disadvantages, costs, and maturity of various existing and innovative sediment remedial technologies, see Table 4-6 in the “Implementation Guide for Assessing and Managing Contaminated Sediment at Navy Facilities” (Naval Facilities Engineering Command, 2003) and references listed in that document. While a growing list of treatment technologies is available for sediments, the costs of many of these preclude use at most sites. Many treatment technologies that have been reported at lower cost (e.g., Stern et al., 1994; Detzner, 1992) rely on two things for cost-effectiveness: (1) economy of scale—these technologies are applied at sites where large volumes of fairly uniform sediment are expected to be treated over long periods of time, and (2) a market for an end-product. Costs

are generally calculated assuming a market for by-products such as bricks, aggregate, compost, etc. For most U.S. Navy sites reviewed in this project, neither factor applies. In general, DoD sites are relatively small, heterogeneous sites. Treatment, if carried out, will probably be for one site at a time. Thus, the costs of technology mobilization, demobilization, fine-tuning, etc., are proportionately high. While this situation may be offset somewhat if regional treatment centers are built, as yet, there is little evidence of such regional, cross-organizational coordination. However, technologies are being developed and marketed continually, and should be considered at appropriate sites, with a careful consideration of the assumptions applied in a vendor's cost estimates.

One technology that was extensively investigated for its potential cost savings is particle separation for volume minimization. In such an investigation, sediments are separated as a function of grain size and/or density (Galloway, 1992), and contaminant and mass distribution in the various fractions is evaluated. If it is determined that the bulk of contaminant reside in a separable sediment fraction that is a relatively small portion of the total sediment volume, in some cases, particle separation will prove cost-effective. In such a case, the result is a smaller volume of highly contaminated sediment, and a large volume of sediment that is relatively uncontaminated, and can be used or disposed of without restrictions. In most U.S. Navy marine sediments examined, a few problems were encountered: (1) in some sediments, all or some of the COPCs had bimodal or even distribution—they did not just reside in just one fraction; (2) in some sediments, different COPCs were distributed among different fractions; (3) contaminant levels were relatively low, so those that exceeded SQGs due to fraction-associated COPCs only did so in sediments with a high proportion of that size or density fraction, thus, separation would not significantly reduce volumes; and (4) for most sediments examined, disposal costs were too low to justify pre-treatment costs. However, these factors will not apply to all sediments, so [SOP 3](#) illustrates the methods for separating and evaluating contaminant distribution, and [SOP 4](#) illustrates the methodology for evaluating potential cost savings as a function of pre-treatment. In such cases where disposal options are severely limited or prohibitively expensive, pre-treatment should be considered. For large sites such as Hamburg Harbor, this approach provides significant savings of cost and is extending the life of limited disposal sites. **Case Study 11** illustrates a case in which sediment characteristics may justify a cost-savings evaluation. At this site, dredging one small operating unit (OU C) was evaluated as a possible remedy to reduce risk from the principal COPC, Cu. Two important criteria for assessing this remedial option were the evaluations of volume reduction and costs. In this case study, further analysis was performed to determine the effects of pre-treatment on the volume of dredged sediment and overall treatment costs. Size separation was selected as the pre-treatment choice for this site. Size separation analysis of the collected cores revealed that 25% of the total sediment mass within OU C consisted of fine-grained sediment (<0.063 mm), while metals analysis showed that this fine-grained sediment accounted for 80% of the Cu mass within OU C. Calculations were performed ([see SOP 4, Appendix A](#)) to determine the effects of separating the size fractions of OU C on the overall treatment costs (C_t). The first table shows the overall costs incurred during and after the size separation process. In this case study, the coarse-grained fraction remaining after size separation (75 % of the original mass) contained levels of Cu consistent with ocean disposal levels. Therefore, treatment costs were mainly associated with the disposal of this low-level contaminated sediment. The disposal unit cost (C_d) represented the disposal costs of the highly contaminated sediment removed after size separation (in this case, the fine-grained sediment representing 25% of the original mass).

For comparison, the second table shows the costs for bypassing pre-treatment and dredging the entire OU C. In this case study, a 10% cost reduction was created by removing the contaminated fine-grained fraction. For the volume of sediment within OU C (surface area of 1 acre and depth of 0.67 yd = 3227 cu yd), this removal would save \$32,000.

CASE STUDY 11: PRE-TREATMENT OF COST EVALUATION

Core samples were collected at various locations of this site. Using ER-M as the selected benchmark, Cu was flagged as a COPC in the upper right portion of the basin. Dredging this small operating unit (OU C) was evaluated as a possible remedy to reduce risk. Two important criteria for assessing this remedial option were the evaluations of volume reduction and costs. In this case study, further analysis was performed to determine the effects of pre-treatment on the volume of dredged sediment and overall treatment costs. Size separation was selected as the pre-treatment choice for this site.

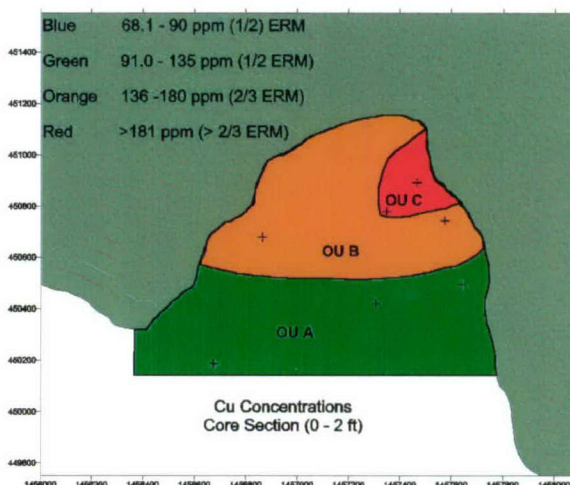


Figure 17-1. Depth Cu concentration within OUs A through C.

Size separation analysis of the collected cores revealed that 25% of the total sediment mass within OU C consisted of fine-grained sediment (< 0.063 mm), while metals analysis showed that this fine-grained sediment accounted for 80% of the Cu mass within OU C.

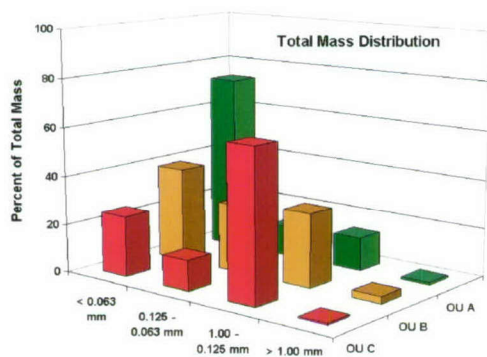


Figure 17-2. Sediment size fraction distribution within OUs A through C.

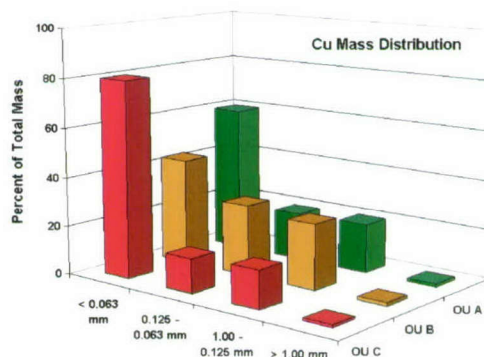


Figure 17-3. Cu size fraction distribution within OUs A through C.

CASE STUDY 11 (continued)

Calculations were performed (see SOP 4; Appendix A) to determine the effects of separating the size fractions of OU C on the overall treatment costs (C_t). The overall costs incurred during and after the size separation process are shown in the first table. The pre-treatment unit cost (C_p) represented the cost of separating the size fractions of the sediment. The final treatment unit cost (C_f) represented the costs associated with the treatment of sediment remaining at the site. In this case study, it was determined that the coarse-grained fraction remaining after size separation (75% of the original mass) contained levels of Cu consistent with ocean disposal levels. Therefore, treatment costs were mainly associated with the disposal of this low-level contaminated sediment. The disposal unit cost (C_d) represented the disposal costs of the highly contaminated sediment removed after size separation (in this case, the fine-grained sediment representing 25% of the original mass). For comparison, Figure 17-5 shows the costs for bypassing pre-treatment and dredging the entire OU C.

Overall Treatment Costs with Pretreatment

C_p = pretreatment unit cost (\$15-75/cu yd)	\$50
C_f = final treatment unit cost (\$0 - 1000/cu yd)	\$20
C_d = disposal unit cost (\$0 - 100/cu yd)	\$100
m = unit mass removed after pretreatment	0.25
C_t = total treatment unit cost $C_p + ((1 - m) \cdot C_f) + (m \cdot C_d)$	\$90

Figure 17-4. Sample calculation of total treatment costs including pre-treatment (size-separation).

Overall Treatment Costs without Pretreatment

C_d = disposal unit cost (\$0 - 100/cu yd)	\$100
m = unit mass removed after pretreatment	1.00
C_t = total treatment unit cost $C_p + ((1 - m) \cdot C_f) + (m \cdot C_d)$	\$100

Figure 17-5. Sample calculation of total treatment costs (disposal only).

In this case study, a 10% cost reduction was created by removing the contaminated fine-grained fraction. For the volume of sediment within OU C (surface area of 1 acre and depth of 0.67 yd = 3227 cu yd), this removal would save \$32,000.

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APPENDIX A: SEDIMENT CHARACTERIZATION STANDARD OPERATING PROCEDURES (SOPS)

SOP 1: Mass Allocation of Sediment and Contaminant

In many cases, it is possible to perform mass balance calculations in the area of concern. Not only can contaminant concentration in given sediment units be determined, but the relative distribution of contaminants throughout the area of concern, in absolute terms and relative to selected benchmarks, can be calculated. This information will allow risk managers to begin to frame the feasibility and potential consequences of various management options. The following SOP describes the assumptions and calculations used to conduct these comparisons.

1. Define the borders of the area of concern. The COPC concentrations data are most useful in delineating the size of the area of concern.
2. If applicable, delineate smaller sediment operating units (OUs) within the area of concern. OUs (Figure A-1) are subgroups (i.e., strata) that are internally homogeneous and distinct when compared to the heterogeneous area of concern. The number of OUs within the area of concern will depend on the characteristics of the site and the availability of data.

(Equation 1)
$$\text{Area of Concern} = \sum_{i=1}^N \text{OU}_i ,$$

where N is the number of OUs within the area of concern.

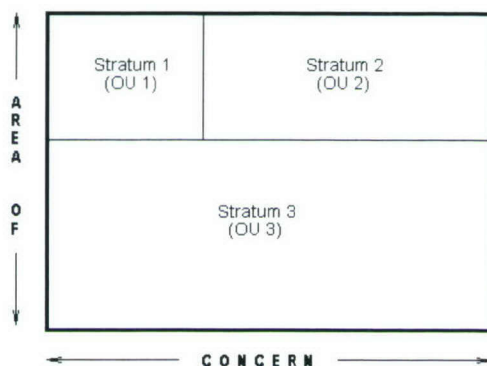


Figure A-1. Delineation of OUs within the area of concern.

3. The main application of the mass allocation equations is to characterize whole volumes of sediments. To calculate sediment volume, the depth of contaminated sediment within the area of concern must be determined.

Core samples are the most common method of delineating the contaminant depth profile within the site. Figure A-2 shows the cross section of a core sample taken from OU_i. In this example, L_{Ti} represents the depth of contaminated sediment. The contaminant concentrations ([A_{1i}], [A_{2i}], ..., [A_{Xi}]) are measured for X layers (L_{1i}, L_{2i}, ..., L_{Xi}) of the core sample to calculate its contaminant depth profile. The contaminant depth profile will be used in future mass allocation equations.

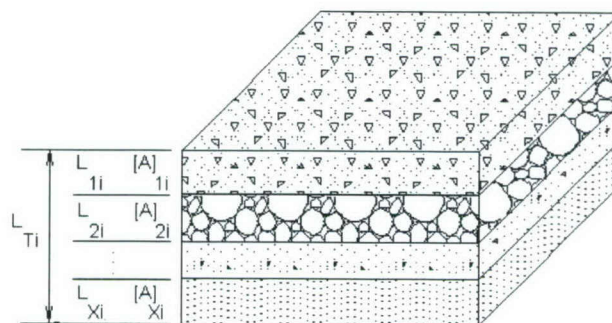


Figure A-2. Cross section of a core sample.

4. Create a hypothetical box containing the contaminated sediment of interest. The depth of contaminated sediment and the size of the area of concern are used to define the volume of this box. The mass allocation equations in this SOP will examine the relative and absolute distributions of sediment and contaminant within this hypothetical box.
5. Calculate the mass of sediment in each OU. Because contaminant levels in the sediments will be compared with a number of potential benchmark values, all of which are reported in dry weight units, an initial step is to put the mass of sediments in each OU in terms of dry weight. The following describes the calculations used:

First, the volume of sediment in each OU (V_i , in m³) is calculated, by the following equation:

(Equation 2)
$$V_i = L_{Ti} \times S_i,$$

where L_{Ti} is the depth of contaminated sediment (m) and S_i is the surface area^{A-1} (m²) of OU_i.

Next, the sediment is converted to dry weight volume:

(Equation 3)
$$V_{Di} = V_i \times P_i,$$

where V_{Di} is the volume of sediment in OU_i dry (m³), and P_i is the % solids of OU_i^{A-2}.

The mass of sediment in each OU can then be calculated:

(Equation 4)
$$M_{Di} = V_{Di} \times \rho_i \times \frac{cm^3}{(10^{-2}m)^3} \times 10^{-3} kg / g,$$

where M_{Di} is the weight of sediment in OU_i (kg dry weight), and ρ_i is OU_i sediment density (g/cm³)^{A-3}.

^{A-1} Surface area can be calculated with Trimble Pathfinder Office[®] Software (Trimble Inc.) based on map coordinates.

^{A-2} Measured by percent weight before and after drying at 105° C.

^{A-3} Measured by BET analysis (dry bulk sediments).

The relative mass distribution of each OU can then be calculated to show its contribution to the entire area of concern:

$$(Equation\ 5) \quad M_{Ri} = \frac{M_{Di}}{\sum_{j=1}^N M_{Dj}} \times 100,$$

where N is the number of OUs within the area of concern.

6. Once the sediment masses have been calculated, they can be multiplied by contaminant (COPC) concentrations within a given OU to determine total mass in kilograms of a contaminant that can be attributed to that OU.

The concentration depth profile found in Step 3 of this SOP can be used in the following equation to determine total mass of a COPC attributed to a given OU:

$$(Equation\ 6) \quad M_{Ai} = \sum_{j=1}^X ([A]_{ji} \times (M_{Di} \times \frac{L_{ji}}{L_{Ti}})),$$

where M_{Ai} is the total mass of contaminant **A** in OU_i sediments (kg dry weight), X is the number of layers within the concentration depth profile of OU_i , $[A]_{ji}$ is the concentration of contaminant **A** measured in the j^{th} layer of OU_i , L_{ji} is the thickness of the j^{th} layer of OU_i , and L_{Ti} is the total depth of the contaminated sediment.

The relative distribution of a particular contaminant throughout the site can then be calculated to show the contribution of each OU to the contaminant loading in the area of concern:

$$(Equation\ 7) \quad M_{RAi} = \frac{M_{Ai}}{\sum_{j=1}^N M_{Aj}} \times 100,$$

where N is the number of OUs within the area of concern.

7. Additional equations used in mass allocation examine the relative distributions of contaminants exceeding selected benchmarks or Sediment Quality Guidelines (SQGs) such as regional ambient levels. This examination will provide insight into the relative distribution of a proportion of the contaminant load, which might plausibly be managed, or of concern. For a given OU, it is first necessary to determine the degree of exceedance of a given COPC to a given benchmark:

$$(Equation\ 8) \quad E_{Ai} = M_{Ai} - ([SQG]_A \times M_{Di}),$$

where E_{Ai} is the weight (kg) of contaminant **A** in excess of the amount it would be at a given benchmark and $[SQG]_A$ is the concentration of contaminant **A** for a given benchmark (ambient or reference level, ER-L, ER-M, RR, etc.).

If E_{Ai} in the previous equation is negative, the amount of COPC within the OU does not exceed the amount it would be at the benchmark level. In this case, $E_{Ai} = 0$.

Once the degree of exceedance has been determined for all the OUs, the relative distribution of COPC **A** exceeding a given criterion or level can be determined:

(Equation 9)
$$E_{RAi} = \frac{E_{Ai}}{\sum_{j=1}^N E_{Aj}} \times 100 ,$$

where E_{RAi} is the percent distribution of contaminant **A** in exceedance of a given benchmark in OU_i relative to the entire area of concern, and N is the number of OUs within the area of concern.

8. Pie charts can assist in visualizing the results of the mass allocation calculations performed in Equations 5, 7, and 9. These charts help in evaluating the relative loading of contaminants in a region. They can also help in determining the potential impact to total loading if given sediment volumes are contained, controlled, or removed.

SOP 2: Potential Effects of Long-Term Mixing on COPC Concentrations

It is possible to calculate the potential impact of contaminant levels in the area of concern if the sediments were completely mixed. These calculations can be done with all the sediment, and with selected units removed. Variables that may affect these calculations are the selection of the COPC and the type of data available for the area of concern. Of course, this calculation is just an “end-member” calculation—it is extremely improbable that an entire site would ever be mixed. However, if sediments are left in place with uncontrolled future activities, it is plausible that some unknown degree of mixing, resuspension, and transport may occur. These calculations only predict improbable extremes, to assess some risks, benefits, or consequences of leaving sediments in place with no controls.

1. Determine if the COPC (risk driver) is a strong bioaccumulator (i.e., PCB). If it is a strong bioaccumulator, consider exiting this SOP because dispersion is a problem. Dispersion in the short term can result in a transitory state with larger volumes of sediment of concern. The short-term effects of this COPC dispersion will supersede management decisions based on long-term mixing calculations. If the COPC is not a strong bioaccumulator, continue to the next step.
2. Define the borders of the area of concern. The COPC concentrations data are most useful in delineating the size of the area of concern.
3. If applicable, delineate smaller sediment operating units (OUs) within the area of concern. OUs (Figure A-5) are subgroups (i.e., strata) that are internally homogeneous and distinct when compared to the heterogeneous area of concern. The number of OUs within the area of concern will depend of the characteristics of the site and the availability of data.

(Equation 1)
$$\text{Area of Concern} = \sum_{i=1}^N SMU_i ,$$

where N is the number of OUs within the area of concern.

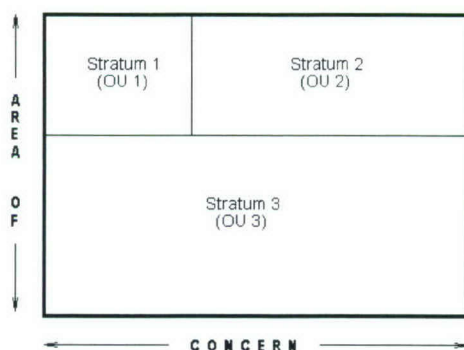


Figure A-3. Delineation of OUs within area of concern.

The mixing equations in this SOP will examine the effect of mixing after hypothetically removing or containing selected OUs from the area of concern.

4. Determine the hypothetical mixing depth of the sediment that will be disturbed during an extreme event.
5. Create a hypothetical box containing the contaminated sediment of interest. The hypothetical mixing depth and the size of the area of concern define the volume of this box. The mixing equations in this SOP will examine the effect of mixing on the sediments contained within this hypothetical box.
6. The first step in using the mixing equations is to calculate the mass of sediment in each OU. Because contaminant levels in the sediments will be compared with a number of potential benchmark values, all of which are reported in dry weight units, an initial step is to put the mass of sediments in each OU in terms of dry weight. The following describes the calculations used:

First, the volume of sediment in each OU (V_i , in m^3) is calculated by the following equation:

(Equation 2)
$$V_i = L_{Ti} \times S_i,$$

where L_{Ti} is the hypothetical mixing depth (m) and S_i is the surface area^{A-4} (m^2) of OU_i.

Next, the sediment is converted to dry weight volume:

(Equation 3)
$$V_{Di} = V_i \times P_i,$$

where V_{Di} is the volume of sediment in OU_i dry (m^3), and P_i is the % solids of OU_i^{A-5}.

The mass of sediment in each OU can then be calculated:

(Equation 4)
$$M_{Di} = V_{Di} \times \rho_i \times \frac{cm^3}{(10^{-2}m)^3} \times 10^{-3} kg / g,$$

where M_{Di} is the weight of sediment in OU_i (kg dry weight), and ρ_i is OU_i sediment density (g/cm^3)^{A-6}.

7. Once the sediment masses have been calculated, they can be multiplied by contaminant (COPC) concentrations within a given OU to determine total mass in kilograms of a given contaminant that can be attributed to a given OU.

If only surface contaminant data are available, use the surface concentration in the following equation:

(Equation 5)
$$M_{Ai} = [A]_i \times M_{Di},$$

where M_{Ai} is the total mass of contaminant **A** in OU_i sediments (kg dry weight) and $[A]_i$ is the measured surface concentration of contaminant **A** in OU_i sediment sample.

However, if the contaminant profile is known within the mixing zone, the previous equation can be refined. Figure A-4 shows the cross section of OU_i found within the hypothetical box.

^{A-4} Surface area can be calculated with Trimble Pathfinder Office® Software (Trimble Inc.) based on map coordinates.

^{A-5} Measured by percent weight before and after drying at 105° C.

^{A-6} Measured by BET analysis (dry bulk sediments).

In this example, the depth profile $(L_{1i}, [A]_{1i}), (L_{2i}, [A]_{2i}), \dots, (L_{Xi}, [A]_{Xi})$ is known along the length of the mixing depth (L_{Ti}) .

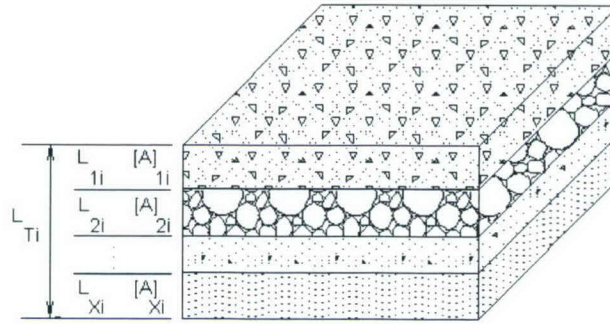


Figure A-4. Cross section of OU_i .

In this case, use the concentration depth profile in the following calculation:

(Equation 6)
$$M_{Ai} = \sum_{j=1}^X ([A]_{ji} \times (M_{Di} \times \frac{L_{ji}}{L_{Ti}})),$$

where M_{Ai} is the total mass of contaminant **A** in OU_i sediments (kg dry weight), $[A]_{ji}$ is the concentration of contaminant **A** measured in the j^{th} layer of OU_i , L_{ji} is the thickness of the j^{th} layer of OU_i , and L_{Ti} is the total length of the hypothetical mixing depth.

8. The first mixing equation determines the weighted average COPC concentration within the hypothetical box. Essentially, this concentration of a COPC would be expected if the sediments within the entire area of concern were mixed.

Remember, the area of concern is the sum of the OUs defined in Step 3. Therefore, the sediment and contaminant masses of each OU must be added together to calculate the total mass of sediment and contaminant within the area of concern (Equation 7):

(Equation 7)
$$[A]_{wt} = \frac{\sum_{i=1}^N M_{Ai}}{\sum_{i=1}^N M_{Di}},$$

where $[A]_{wt}$ is the weighted average concentration of contaminant **A** in the entire area of concern.

This weighted average concentration can now be compared with potential benchmark values. Again, this mixing calculation only predicts improbable extremes to assess some risks, benefits, or consequences of leaving sediments in place with no controls.

9. Next, the weighted average concentration of a COPC within the area of concern, if a given unit or units were removed, contained, or sequestered, and the rest of the area that were mixed, can be calculated:

(Equation 8)

$$[A]_{wp(-1)} = \frac{\sum_{i=2}^N M_{Ai}}{\sum_{i=2}^N M_{Di}}, \text{ and so forth,}$$

where $[A]_{wp}$ is the weighted average concentration of contaminant A in the area of concern, assuming 1 or more OUs are removed.

Again, the weighted average concentration can be compared with potential benchmark values to evaluate the effects of hypothetically removing or containing selected OUs.

SOP 3: Size Fraction Contributions to Bulk Metal Concentration

If sediment is determined to be of either ecological or regulatory concern, this determination is probably based on levels of COPCs that exceed a regulatory benchmark, literature, or site-specific toxicity threshold. However, it is not the bulk concentration of a contaminant that poses risk, but the fraction of that bulk concentration that is bioavailable. Thus, in assessing risk or a risk management approach for a specific COPC, determining the form in which the COPC resides in the sediment can be very important. Size fraction distribution *can* be one indicator of potential differences in availability or risk. The following equations use sediment concentration and fractions data to determine the contributions of specific sediment fractions to bulk contaminant load. One application of this analysis is the determination of specific sediment fractions that could be expected to account for the exceedance of a chosen benchmark. In cases where one particular fraction may be more or less bioavailable than another, this case may indicate that one portion of the COPC load can be discounted (e.g., if the fraction contains a highly bound or natural fraction) or given particular weight (e.g., if the fraction is clearly mobile, as in anti-fouling paint-bound metals).

1. Define the categories of size fractions of interest. Typically, for engineering purposes, the fine-grained fractions are defined as less than 63 μm and the coarse-grained fraction greater than 63 μm . Other size fractions may be selected based on site information, historical information about a specific particle source, etc.
2. Perform grain size separation and analysis of the sediment sample. The most common method of determining grain size distribution, with size separation (as opposed to an optical method that does not separate samples during analysis), is sieving an aliquot of the sediment through a number of sieves. The mesh diameters of this sieve stack should encompass the size fractions of interest. Other methods include stokes settling, hydrocyclone, and reverse flow separation.
3. For each defined size fraction, measure COPC concentrations and the mass of dry sediment within the size fraction.
4. Convert the COPC concentrations in a given size fraction (in units of mg/kg in this example) to a total amount of the COPC (mg) in each size fraction for a theoretical kg of sediment. The amount of COPC in each size fraction, defined as M_m , is calculated:

(Equation 1)
$$M_m = C \times M_f,$$

where C = the concentration of COPC measured in the size fraction (mg/kg) and M_f = the mass of dry sediment in the size fraction (kg).

5. The sum of the COPC masses from all the defined size fractions gives the total mass of COPC (M_t) within the sample:

(Equation 2)
$$M_t = \sum_{\text{fractions}} M_m$$

6. The amount of COPC in each fraction, in terms of percentage of the total mass, can be defined as P_m and calculated:

(Equation 3)
$$P_m = \left(\frac{M_m}{M_t} \right) \times 100$$

7. The COPC concentration contribution of each size fraction, defined as C_f , can now be calculated using the bulk COPC concentration and P_m :

(Equation 4)
$$C_f = \frac{(C_b \times P_m)}{100},$$

where C_b is the bulk COPC concentration of the sediment.

The concentration contribution of each defined size fraction can be plotted as a stacked bar graph to assist in interpreting results. When plotted next to selected benchmarks, the calculation of concentration contribution can show if a specific size fraction accounts for the exceedance of a chosen benchmark.

SOP 4: Effect of Pre-treatment on Overall Treatment Cost

One factor in comparing remedial alternatives is evaluating the site-specific cleanup values of the contaminated sediment. For example, if dredging is proposed for an area of concern, site-specific data can be fed into cost equations to determine if the contaminant distribution of the sediment justifies particle separation. If cost evaluations validate the use of this form of sediment pre-treatment, the contaminated sediment can be separated from uncontaminated sediment before any other treatment, containment, or disposal options are started. The resulting reduction of sediment volume requiring management would play a critical part in cost control. This SOP looks at the equations used to evaluate the effect of pre-treatment (in this case, separating contaminated from uncontaminated sediment) on the overall treatment cost.

1. Define the categories of size fractions of interest. Typically, for engineering purposes, the fine-grained fractions are defined as less than 63 μm and the coarse-grained fraction greater than 63 μm . Other size fractions may be selected either based on site information, historical information about a specific particle source, etc.
2. Perform grain size separation and analysis of the sediment sample. The most common method of determining grain size distribution with size separation (as opposed to an optical method that does not separate samples during analysis) is sieving an aliquot of the sediment through a number of sieves. The mesh diameters of this sieve stack should encompass the size fractions of interest. Other methods include stokes settling, hydrocyclone, and reverse flow separation.
3. For each defined size fraction, measure COPC concentrations and the mass of dry sediment within the size fraction (m_i).
4. The sum of the dry sediment masses from all the defined size fractions gives the total mass of dry sediment (m_t) within the sample:

(Equation 1)
$$m_t = \sum_{\text{fractions}} m_i,$$

where m_i is the dry sediment mass within the i^{th} size fraction.

The relative mass distribution of each size fraction can then be calculated to show its contribution to the entire sample:

(Equation 2)
$$P_i = \frac{m_i}{m_t},$$

where P_i is the relative mass component of the i^{th} size fraction.

5. Examination of the COPC concentrations within each size fraction assists in determining whether contaminants are associated with a certain grain size. If the bulk of contaminants reside in the i^{th} size fraction, the contaminated sediment might be a candidate for separation. If this size fraction were selected for pre-treatment and separated from the sediment, the amount of a unit mass of sediment removed after pre-treatment (M) is calculated:

(Equation 3)
$$M = P_i,$$

where P_i is the relative mass component of the size fraction chosen for pre-treatment.

6. Cost equations are used to determine if contaminant distribution justifies separation on a cost and volume basis. These equations incorporate treatment and disposal costs, as well as the mass of sediment affected by pre-treatment.

The total treatment cost, on a per unit basis, (C_T), is calculated:

(Equation 4)
$$C_T = C_P + (1 - M)C_F + MC_D,$$

where C_P is the pre-treatment unit cost, C_F is the final treatment unit cost, C_D is the disposal unit cost, $(1-M)$ is the sediment unit mass remaining after pre-treatment, and M is the sediment unit mass removed after pre-treatment.

7. The effect of pre-treatment on the overall treatment cost can be quantified by examining the cost difference in the total treatment cost of separating sediment versus the disposal cost of the unseparated bulk sediment:

(Equation 5)
$$\Delta C = (C_D - C_T) \times V,$$

where ΔC is the difference in cost and V is the volume of sediment (yd^3) being managed.

APPENDIX B: SEDIMENT CHARACTERIZATION FLOWCHARTS

CHART 1: BACKGROUND CONSIDERATIONS FOR METAL COPCS

**Chart 1: Step 3a: Refinement of Conservative Exposure Assumptions;
Background Considerations for Metal COPCs**

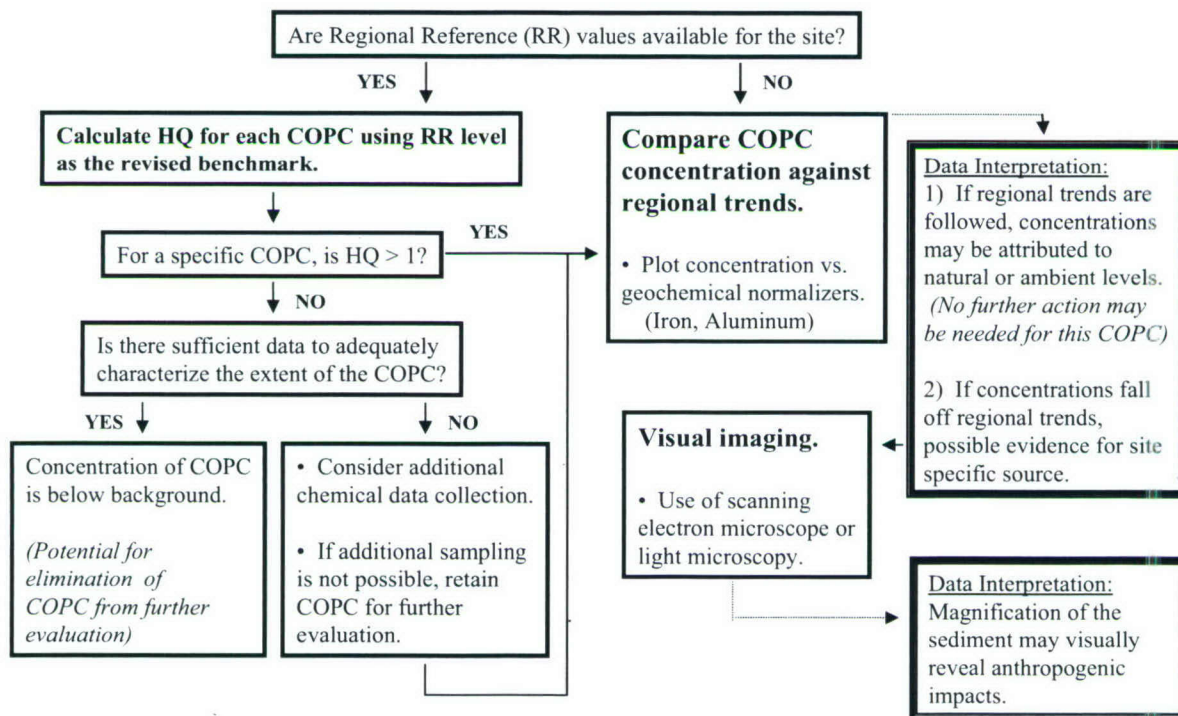


CHART 2: BACKGROUND CONSIDERATIONS FOR ORGANICS COPCS

**Chart 2: Step 3a: Refinement of Conservative Exposure Assumptions;
Background Considerations for Organics COPCs**

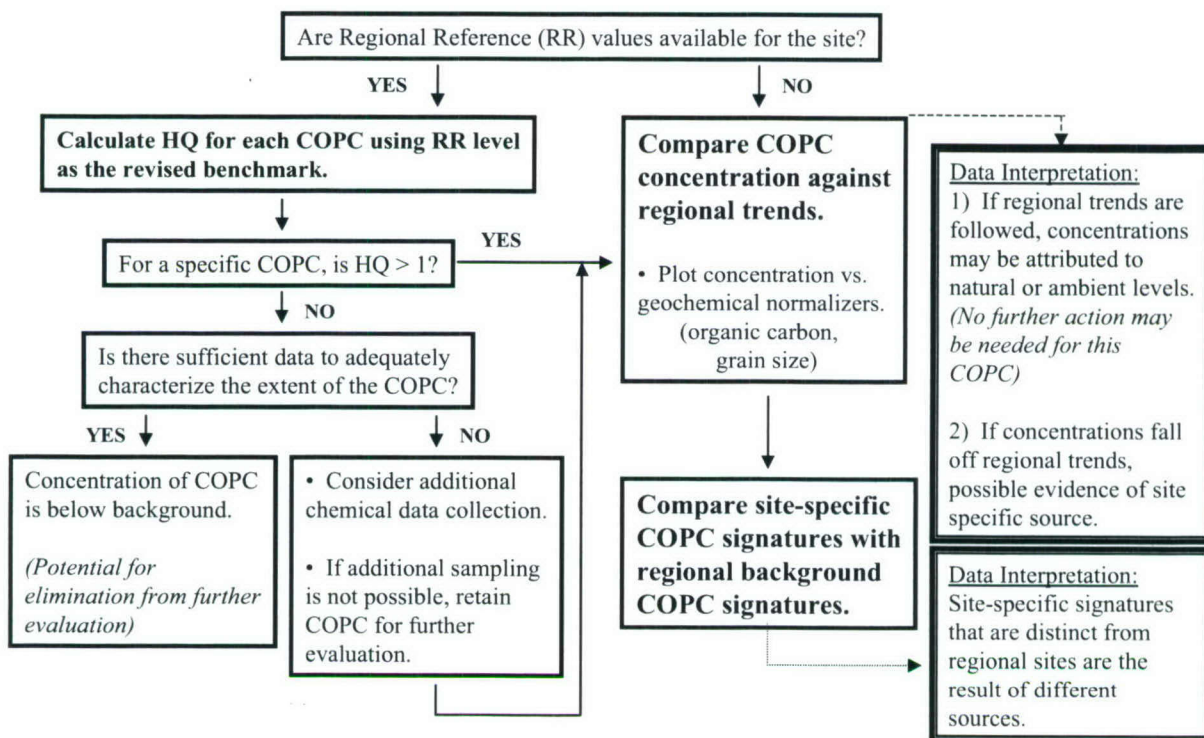


CHART 3: DETECTION FREQUENCY OF COPCS

**Chart 3: Step 3a: Refinement of Conservative Exposure Assumptions;
Detection Frequency of COPCs**

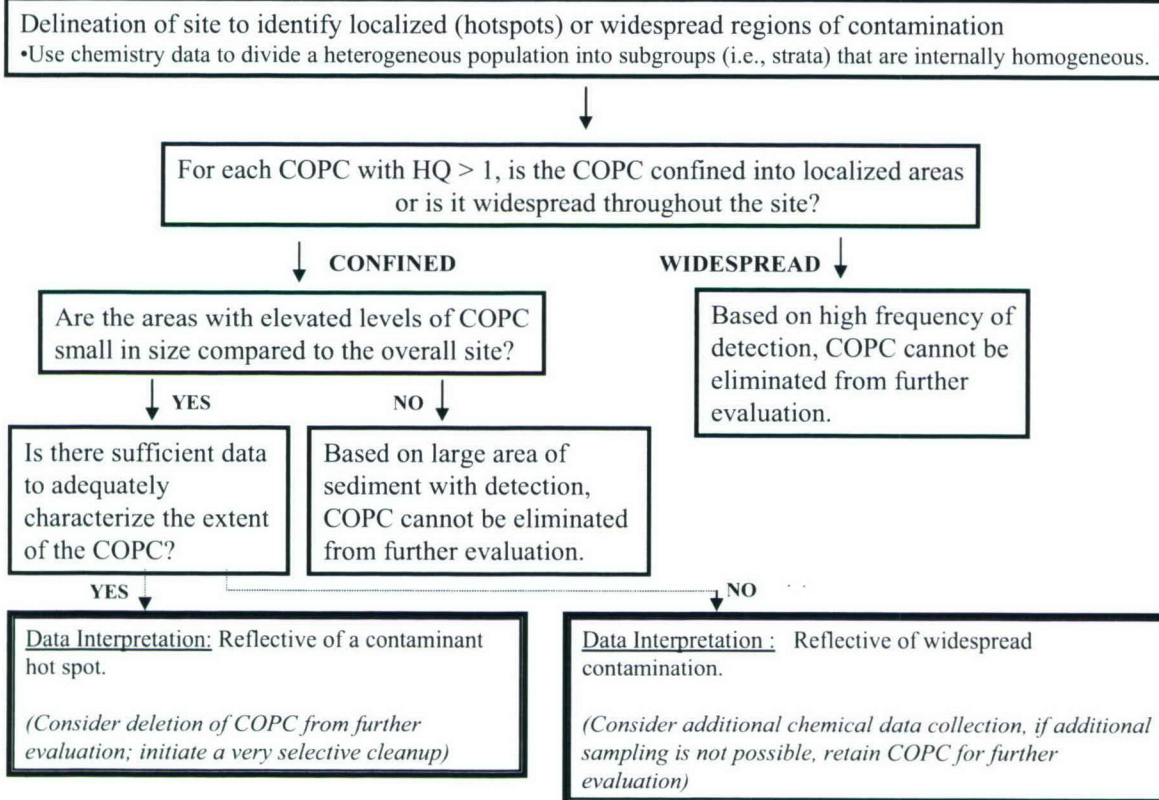


CHART 4: METALS COPC LINES-OF-EVIDENCE

Chart 4: Step 7. Risk Characterization Metals COPC Lines-of-Evidence (LOE)

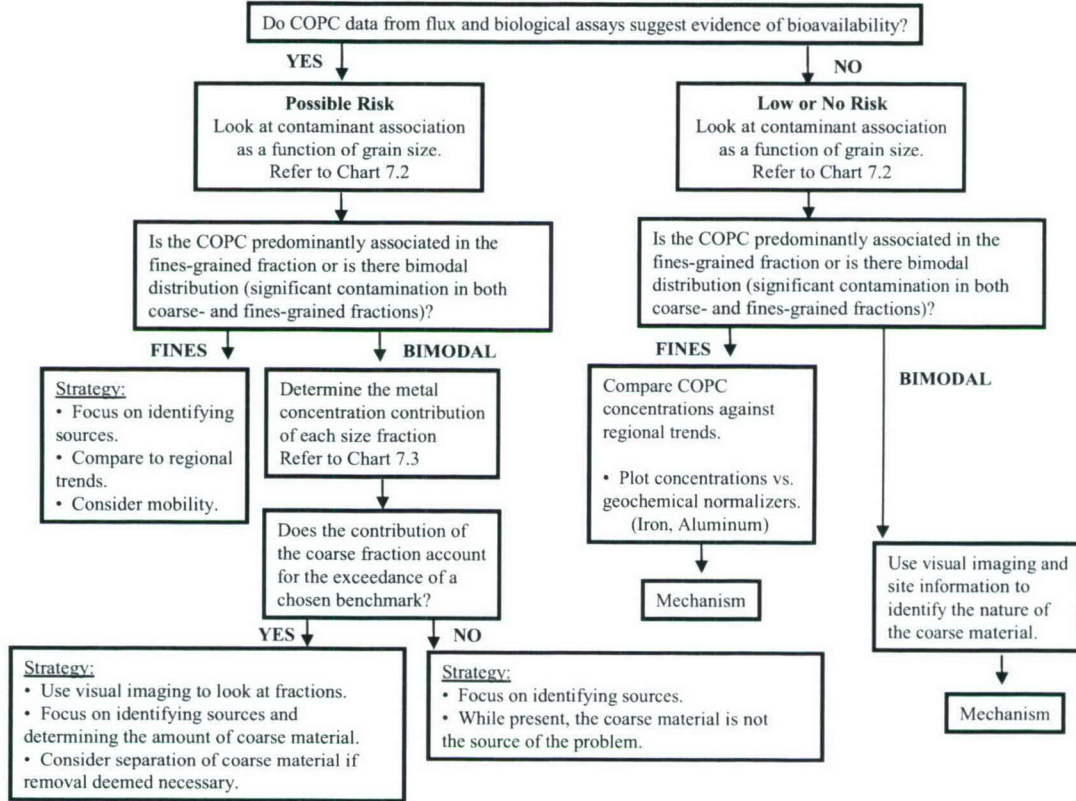
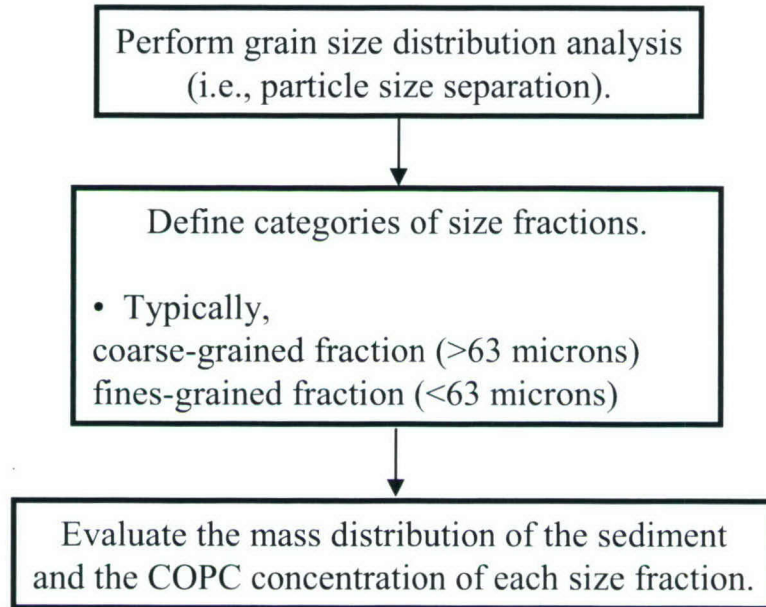


CHART 5: METALS COPC SIZE FRACTION DISTRIBUTION

**Chart 5: Metals COPC Size Fraction
Distribution**



**CHART 6: METALS COPC CONCENTRATION
CONTRIBUTION OF EACH SIZE FRACTION**

**Chart 6: Metals COPC Concentration
Contribution of each Size Fraction**

Normalize COPC fraction concentrations
to the mass distribution of sediment.

- The resulting calculations give the amount
of COPC in each size fraction.



Multiply the amount of COPC in each size
fraction by the bulk COPC concentration.

- The resulting calculations give the metal
concentration contribution of each size
fraction.



Plot concentration contributions as stacked
bar graphs to visual the results.



Visualize

CHART 7: PAH COPC LINES-OF-EVIDENCE (SIZE FRACTION DISTRIBUTION)

Chart 7: Step 7. Risk Characterization PAH COPC Lines-of-Evidence (LOE)
(Size Fraction Distribution)

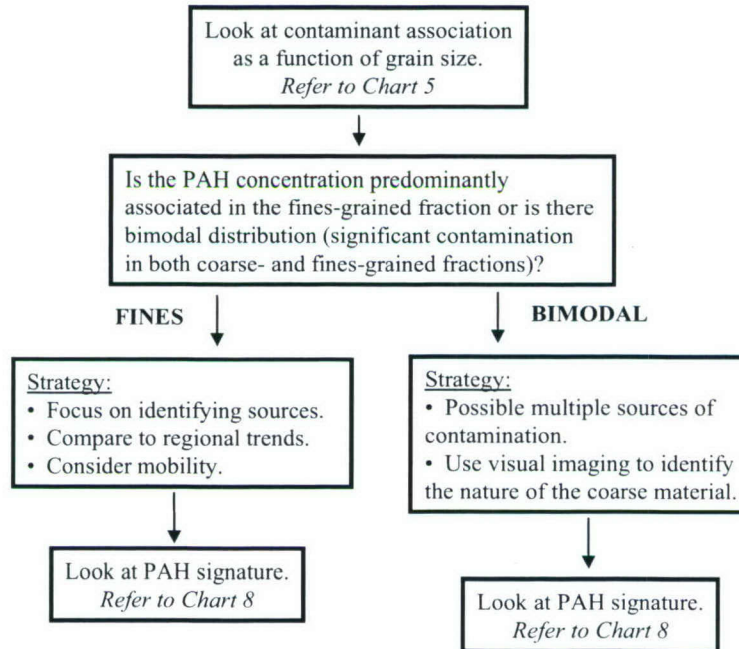


CHART 8: PAH COPC LINES-OF-EVIDENCE (PAH SITE-SPECIFIC SIGNATURES)

Chart 8: Step 7. Risk Characterization
PAH COPC Lines-of-Evidence (LOE)
(PAH Site-Specific Signatures)

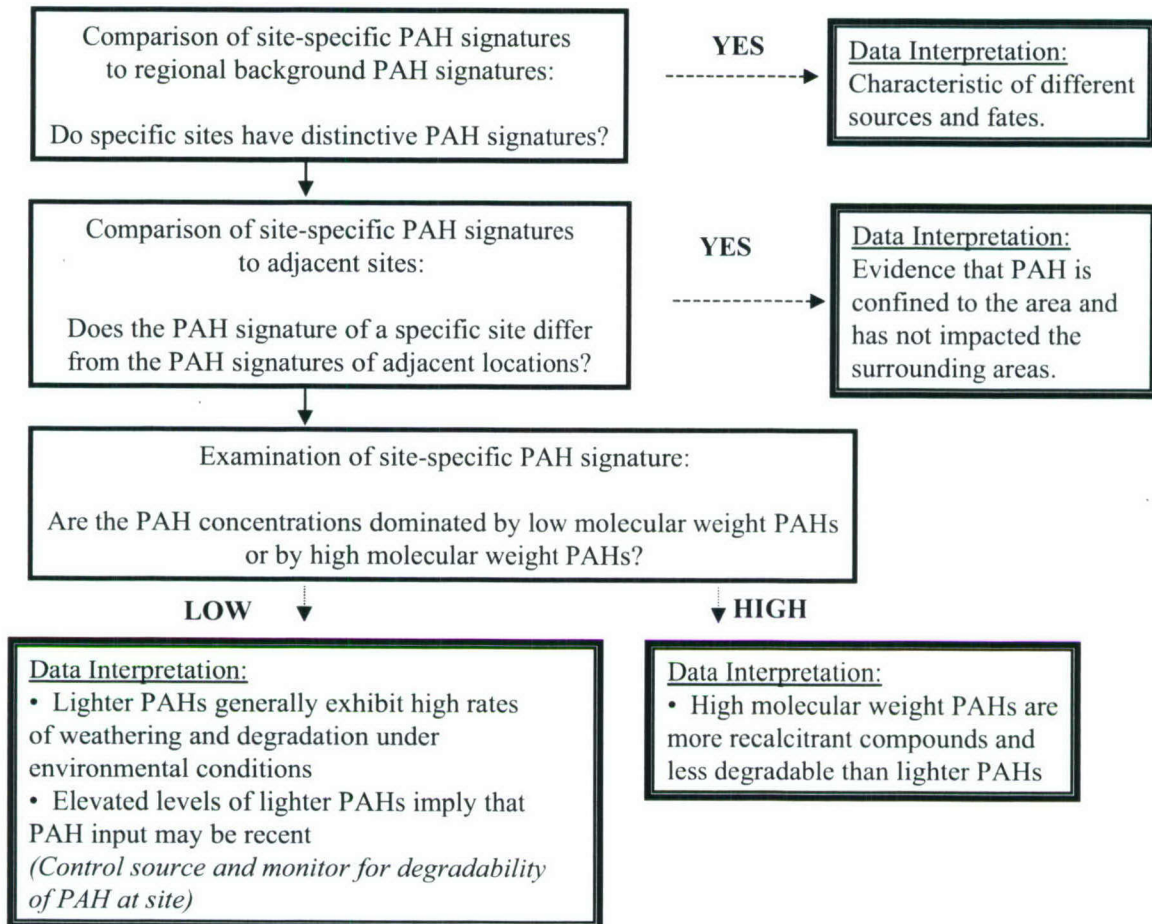
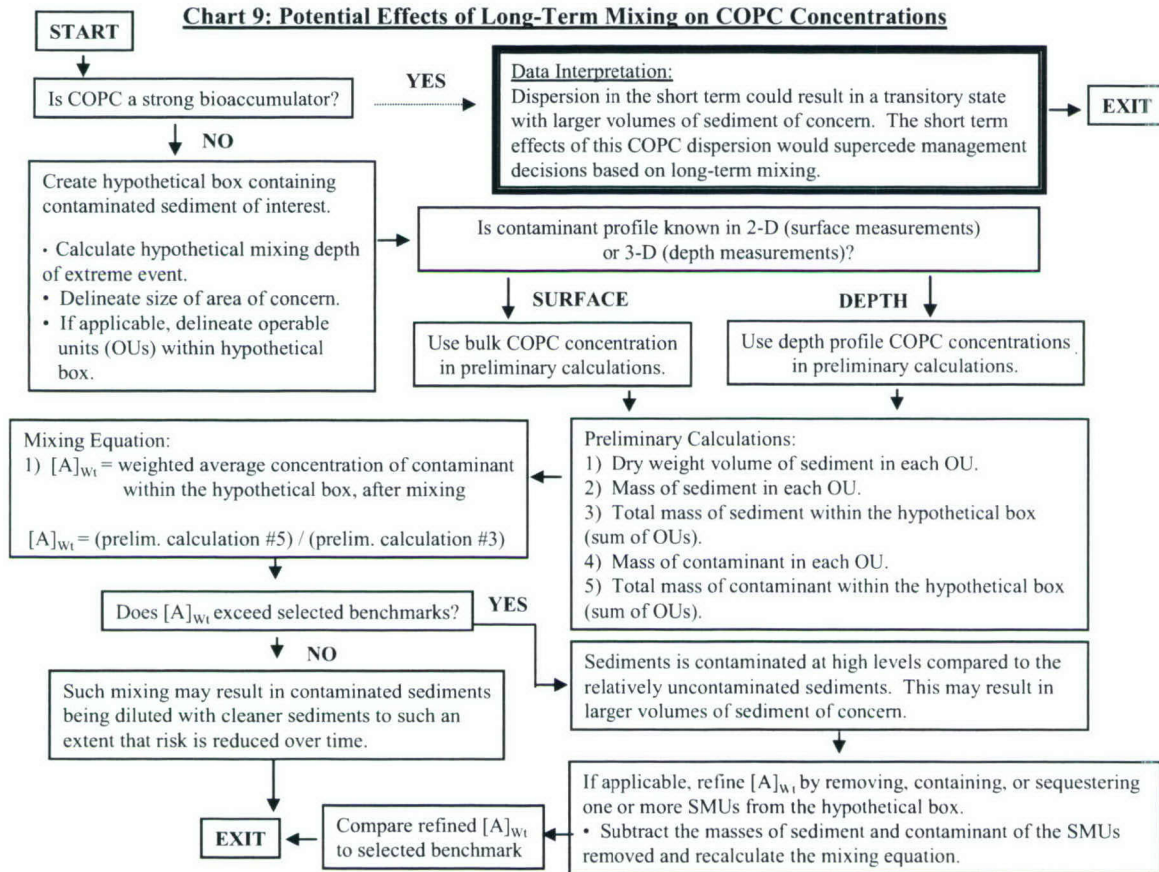


CHART 9: POTENTIAL EFFECTS OF LONG-TERM MIXING ON COPC CONCENTRATIONS



REPORT DOCUMENTATION PAGE

Form Approved
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1. REPORT DATE (DD-MM-YYYY) 08-2004		2. REPORT TYPE Technical		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE USE OF DATA ON CONTAMINANT/SEDIMENT INTERACTIONS TO STREAMLINE SEDIMENT ASSESSMENT AND MANAGEMENT				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHORS S. E. Apitz B P. Ayers V. J. Kirtay				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) SSC San Diego San Diego, CA 92152-5001				8. PERFORMING ORGANIZATION REPORT NUMBER TR 1918	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Naval Facilities Engineering Command Y0187 Navy Pollution Abatement Ashore Technology Demonstration Program Washington Naval Yard, Washington DC 20374-5065				10. SPONSOR/MONITOR'S ACRONYM(S) NAVFAC	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
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14. ABSTRACT This report presents successful ways to use biogeochemical characterization data to optimize sediment site assessment and management. The report highlights many successful aspects of contaminated sediment assessment and management. It provides site owners with examples of how to use site-specific data to compare site, background, and regional sediment signatures to address risk, determine responsibility for inputs, rank sites, and prioritize management; to help bridge the gap between remedial investigations and feasibility studies; and to provide site owners with the tools to rapidly determine what sediment management approaches are feasible for contaminated sediments at their sites—and to use site data to evaluate, communicate, and negotiate management choices. The approach of this report is to highlight some major uses for data on contaminant/sediment geochemical interactions in the assessment and management of contaminated sediments. It is not an exhaustive review of all potentialities, but it does provide many examples, case studies, and standard operating procedures (SOPs) that should aid Remedial Project Managers (RPMs), risk assessors, and managers in using site data to evaluate, negotiate, and select management strategies.					
15. SUBJECT TERMS Mission Area: Environmental Science characterization data sediment site management standard operating procedures sediment site assessment site data environmental cleanup					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			V. J. Kirtay
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